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Title: ADVANCED OXIDATION TECHNOLOGIES FOR
CHEMICAL DEMILITARIZATION

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Advanced Oxidation Technologies for Chemical Demilitarization

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Abstract

This is the final report of a one-year, Laboratory-Directed Research and Development (LDRD) project at the Los Alamos National Laboratory. Our main project objective was to establish a technical basis for future program development in the area of chemical warfare agent destruction using a Los Alamos-developed advanced oxidation process: a two-stage device consisting of thermal packed-bed reactor (PBR) and a nonthermal plasma (NTP) reactor. Various compounds were evaluated as potential surrogates for chemical warfare (CW) agents. Representative effluent mass balances were projected for future comparisons with incinerators. The design and construction of lab-scale PBR/NTP reactors (consisting of a liquid injection and metering system, electric furnace, condensers, chemical traps, plasma reactors, power supplies, and chemical diagnostics) has been completed. This equipment, the experience gained from chemical-processing experiments, process modeling, and an initial demonstration of the feasibility of closed-loop operation, have provided a technical basis for further demonstrations and program development efforts.

Background and Research Objectives

This project is a Laboratory-Directed Research and Development (LDRD) effort in the Program Development (PD) category. It has been focused on potential opportunities for applying new technologies to national problems in chemical demilitarization and establishing a technical basis, centered on a two-stage advanced oxidation process, for building programs in that field.

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In the next several years, the Department of Defense (DoD) has budgeted billions of dollars for chemical demilitarization and the remediation of bases destined for realignment or closure. Safely demilitarizing chemical warfare (CW) agents is a high-priority problem for the DoD. The DoD has been focusing on incineration as a preferred technology for CW-agent destruction because it seems straightforward and because viable alternatives are not available. However, there are strong incentives to apply new ideas to this problem because of the formidable destruction and removal efficiencies (DREs) required for the safe disposal of these compounds, their extreme toxicity, and the concerns related to the drawbacks of incineration (leaks, hazardous air emissions, large secondary waste streams, plugging/damage) and the siting of treatment facilities. Therefore, program-development opportunities exist for demonstrating viable alternatives.

The treatment of these acutely hazardous compounds requires a minimum DRE of six decades (i.e., 99.9999%). Higher levels of destruction are desirable but are practically unobtainable using conventional methods. Closed-loop methods may allow systems to achieve higher DREs more efficiently, while at the same time reducing the risk of unintended atmospheric release. Thermal treatment systems, using oxygen-rich environments, are notoriously difficult to operate in a closed-loop mode. A promising class of methods - advanced oxidation technologies (AOTs) - can serve as a basis for a viable incineration alternative. The terminology AOT is now broadly used for processes involving highly reactive free radicals, some of which may even be reductive rather than oxidative. An AOT, like a nonthermal plasma (NTP)¹, greatly simplifies the system. The system concept of injection into a controlled, recycled gas stream treated with an AOT is much more straightforward than trying to close-loop an incinerator. The concept is to introduce (by volatilization, atomization, or injection) the hazardous chemicals into a selected carrier gas stream and treat the stream with a closed-loop system. This gas stream flows through an NTP unit, where a sizable fraction of entrained contaminant is destroyed. Chemical scrubbers then selectively remove the non-toxic treatment products and pumps recycle the carrier gas back to the starting point. Complete destruction is not required on any given circuit because the scrubbers can be designed to pass on the desired compounds for additional treatment. Makeup or reaction gases can be added to either maintain the desired system pressure or to

promote specific reaction pathways. We have focused on the concept of volatilization/combustion by a thermal packed-bed reactor (PBR), followed by oxidation or reduction in a nonthermal plasma (NTP) reactor. An open-loop PBR/NTP unit has been previously investigated for DOE hazardous waste treatment applications². It operates flamelessly in either oxidative or reductive modes at near-ambient pressure and addresses a large range of chemical forms (liquids, slurries, and pumpable sludges). This marriage of a robust thermal technology with an innovative plasma technology is characterized by improved treatment, reduced emissions, modularity, glovebox compatibility, and an inherent closed-loop architecture. The PBR unit can do similar chemistry to supercritical water oxidation (SCWO) but at near-ambient pressure. This avoids the extreme pressure requirements and attendant risks of SCWO vessels. Our two-stage process is a potential viable alternative to the incineration of CW agents and can be a major advancement for chemical demilitarization.

The project and associated technical work was planned for two years; however program project funding was provided for only one year (FY96). The budget was also reduced in proportion to the LDRD program burden rate at the Laboratory. Therefore, concomitant adjustments in the scope of work were necessarily required. The main adjustment was to concentrate on a single demilitarization concept: combined PBR/NTP reactors for nerve-agent destruction (see Figure 1). Because of the necessary changes in project scope, a second plasma aerosol reactor (PAR) concept that was originally planned could not be explored. However, a related collaborative project with the University of California at Irvine is addressing this concept for solvent-type organic compounds and may address one CW surrogate in FY97.

Importance to LANL's Science and Technology Base and National R&D Needs

This project supports two major Los Alamos Core Technical Competencies - Earth & Environmental Systems and Nuclear Science, Beams & Plasmas, and two Tactical Goals - Working with Industry, and Promoting Great Science. The EM Program Directorate also endorsed an informal thrust area in Advanced Oxidation Technologies (AOTs) for waste management and environmental applications at the time this project was proposed; this project meshes with and supports that thrust. On the national front, this project has provided an

opportunity for Los Alamos researchers to do exciting work in a rapidly-expanding field (AOTs), while building a program to address chemical demilitarization, a very practical and important problem which is receiving increasing national attention.

Scientific Approach and Accomplishments

Background

As discussed above, our main project objective was to establish a technical basis for future program development in the area of chemical warfare agent destruction using a Los Alamos-developed advanced oxidation process (combined PBR/NTP reactors). Figure 1 shows a schematic diagram of the two-stage processing concept. Our approach has been focused on the following tasks: projecting the effluent mass balance for the two-stage unit for comparison with incinerator-based processing, evaluating potential surrogates for CW agents, constructing lab-scale PBR/NTP reactor apparatus, conducting initial chemical-destruction experiments, and carrying out baseline chemical-processing calculations.

Experimental Apparatus

In the two-stage unit, a liquid simulant in a carrier-gas stream (we have employed Ar/O₂ mixtures in the experiments) is injected into the thermal-stage PBR via an atomizer. The PBR volatilizes and/or combusts the simulant via thermal oxidation or pyrolysis and produces off-gases. The PBR off-gas stream is then sent to the NTP unit for further processing via plasma-generated, free-radical reactions. Figure 2 shows a schematic diagram of the experimental setup as configured for open-loop tests. In a closed-loop concept, the NTP reactor effluent would be sent back through the PBR stage. We were not able to carry out a fully closed-loop test (both stages); however, we were able to demonstrate the feasibility of closed-loop operation using the PBR by itself. Figure 3 shows a schematic diagram of the experimental setup as configured for the PBR closed-loop tests. Figure 4 shows a photograph of the two-stage apparatus constructed for this project.

PBR consists of a metal cylinder filled with heated aluminum oxide (alumina) beads, the heat being provided by a surrounding furnace. The dimensions of the PBR used in this project are an inside diameter of 4.4 cm and a heated length of approximately 23 cm.

Spherical alumina beads were employed as the packing material (we used both 6.4-mm and 12.7-mm diameter beads). Figure 5 shows a photograph of the PBR and its associated electric furnace. The PBR stage can treat many hard-to-combust organic liquids over a wide temperature range (300-1300 C), with almost complete combustion taking place at temperatures around 800 - 1,000 C. In most cases, even combustion-resistant compounds can be removed to levels of less than 1 ppm at these temperatures. Remaining contaminants are then removed by the second-stage nonthermal plasma reactor, with its share of waste loading determined by the desired PBR operating temperature. For this project, we have kept a fixed 900 C nominal operating temperature.

Under thermal equilibrium, chemical decomposition in a PBR can be described by the integral equation ³

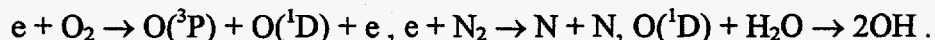
$$V = Q_m \int_0^{R_{out}} \frac{dR}{k[X]}$$

where V is the reactor volume, Q_m is the molar flow rate of the processed compound, R_{out} is the degree of removal at the PBR exit, k is the reaction rate constant, and [X] is the concentration of the subject compound. The reaction rate constant can be described by an Arrhenius expression, $k = A \exp(-E/RT)$, in terms of a reaction constant A, the activation energy E, the gas constant R, and the absolute temperature T, where the values of A and E are specific to the compound being processed. Within this framework, the degree of removal of the processed compound increases exponentially with the reaction temperature. The residence time in the PBR is quite short (approximately 0.4 sec), so combustion/pyrolysis reactions within it do not necessarily proceed to equilibrium. In such cases, the reaction chemistry should be described by a kinetic treatment for more accurate results.

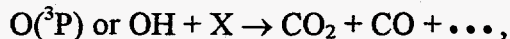
We have employed a silent discharge plasma (SDP) reactor for the second-stage, nonthermal off-gas processor. Silent discharges ⁴ are created at atmospheric pressure by applying a high voltage across dielectric-covered electrodes that enclose a thin (few mm) gas stream. Many transient (few-several ns duration) "microdischarge" current filaments

(streamers) are produced in the barrier discharge configuration. Figure 6 shows a schematic diagram for a single-barrier reactor.

Energetic plasma electrons in such nonthermal-plasma streamers generate highly reactive species (e.g., free radicals) in the gas by reactions such as



Gas-phase pollutants are decomposed by the plasma-generated radicals or secondary electrons. Complex molecules will often undergo a series of reactions before the final products result. Frequently a free-radical-initiation step is dominant in the decomposition process⁵



although strongly electron-attaching molecules (e.g., CCl_4) are preferentially decomposed by dissociative attachment at lower plasma electron temperatures⁶. Nonthermal plasmas show promise for simultaneously treating different types of pollutants such as many volatile organic compounds (VOCs), flue gases (SO_x and NO_x), and other hazardous chemicals^{1,7}. Silent discharges have been previously investigated for applications to military agents.⁸

The key scaling parameter for decomposition is the plasma energy density, or the electrical energy per unit volume deposited in the treated gas (also expressed as the electrical power P deposited in the gas divided by the gas flow rate Q , or P/Q). We normally use units of J/liter or J/cm^3 for P/Q . In many cases, the removal of a pollutant approximately scales as an exponential function of P/Q , so the degree of removal of a given species is given by

$$-\log ([X]/[X]_0) = (P/Q)/\alpha,$$

where $[X]_0$ and $[X]$ are the initial and post-treatment concentrations of species X , respectively and α is the characteristic energy density for one decade removal.

The plasma off-gas stage in our apparatus consists of two double-barrier reactors connected in parallel. Figure 7 shows a photograph of the SDP-cell stack. The cells are housed in a metal tank to control potential emissions, isolate the high voltage connections, and to control mechanical stresses by applying an equalizing gas-pressure in the tank. A heat

exchanger is also used to control the cell temperature. The dielectric barriers are constructed from thin Pyrex sheets. The dimensions of the active cell region are an area of 17.8 cm x 33 cm and a gas-gap spacing of 3 to 4 mm.

Final exhaust gases were discharged through a laboratory stack. Regulated-temperature condensers follow both the PBR and SDP stages. Liquid effluents were collected from the post-SDP condenser for further analysis. Influent and effluent gas samples were connected after the PBR and SDP stages with a combination of a sampling pump and thermal desorption tubes (TDTs). GC/MS (gas chromatograph - mass spectrometer) analysis was employed to analyze the samples. The analytical techniques and results of initial experiments on treating liquids with this system are discussed further below.

Nerve-Agent Surrogates

To simulate the destruction of CW agents in the two-stage system, we needed to identify safe surrogate compounds with similar chemical characteristics to those of real agents. An earlier study⁹ of such simulants provided valuable guidance in narrowing our choices. As previously mentioned, our project focused on nerve agents. Nerve agents are extremely toxic organophosphorous compounds, with GB (also called Sarin) and VX being the two compounds representative of the US stockpile. Based on the referenced study and other literature, we have considered four compounds as useful simulants for these agents: DMMP (dimethyl methyl phosphonate), DIMP (diisopropyl methyl phosphonate), TBP (tributyl phosphate), and the commercial pesticide Malathion. The chemical structures of the two agents VX and GB and the four simulants are shown in Figure 8. The common chemical-structure feature of all the compounds is the presence of a phosphorous-oxygen (P=O) or phosphorous-sulfur (P=S) double bond and two single-bond side groups (such as CH₃, MeO, etc.). In addition to its structure, Malathion is considered an almost ideal simulant because of its very low toxicity. For system shake-down and the development of analytical-chemistry protocols, we found it useful to use a compound of higher volatility than Malathion - methyl ethyl ketone (MEK) was chosen for this.

Mass balances

To provide initial guidance on effluents expected in treating example compounds with our system, as well as with an incinerator, simple stoichiometric-balance calculations for the complete oxidation of the compounds were performed. Table 1 shows the calculated results.

Experimental Conditions and Results

Our main experiments were carried out with the two compounds MEK and Malathion. MEK was employed in both open-loop and closed-loop tests; the Malathion tests were carried out only in an open-loop configuration. The closed-loop tests employed only the PBR stage because of a pressure-differential limit for the SDP cells (a design for higher pressure cells now exists). An Ar/O₂ carrier gas mixture was used in all cases. For open-loop tests, the liquid feed rates for both MEK and Malathion were 0.5 cm³/min at a carrier-gas flow rate of approximately 20 lit/min. For closed-loop tests, the liquid feed rates were 0.25 cm³/min with a carrier-gas flow of approximately 10 lit/min. The nominal PBR temperature was maintained at 900 C for all tests. The SDP plasma energy density was typically 1500 J/lit for the open-loop tests and 2400 J/lit for the closed-loop tests.

For the closed-loop MEK test, the measured O₂ consumption rate was 0.499 g/min versus a calculated consumption rate of 0.495 g/min. For the open-loop Malation test, the measured O₂ consumption is 0.940 g/min versus the calculated consumption rate of 0.895 g/min.

CO₂ was removed using a trap consisting of about 9 kg of dry soda lime (95% calcium hydroxide and 5% sodium and potassium hydroxide). This dry scrubber was of sufficient capacity to remove CO₂ for several days, which is more than adequate for a small scale, developmental unit. The CO₂ level was measured using an IR spectrophotometer and a combustion gas analyzer (CGA). In a large system, the CO₂ could be removed with a bed type scrubber where sodium hydroxide trickles down through the bed to keep it wet. A wet scrubber would be easier to maintain at a constant CO₂ removal rate. The byproduct (sodium carbonate) is soluble in water and has commercial value as a detergent.

Table 1

Mass balances for complete oxidation of example compounds.

	$C_4H_{10}PFO_2$ (GB)	$C_{11}H_{26}NO_2PS$ (VX)	C_4H_{80} (MEK)	$C_3H_9PO_3$ (DMMP)	$C_{12}H_{27}O_4P$ (TBP)	$C_{10}H_{19}O_6PS_2$ (Malathion)	$C_{24}H_{27}PO_4$ (P-ester)
Density (g/cm ³)	1.10	1/01	0.81	1.16	0.98	1.23	1.13
Values below are rates for oxygen consumption and outputs of the listed compounds (in grams/minute).							
O ₂	1.70	4.65	1.98	1.50	2.12	1.79	2.65
CO ₂	1.38	1.83	1.98	1.24	1.94	1.64	2.91
H ₂ O	0.71	0.88	0.81	0.76	0.89	0.64	0.67
P ₂ O ₅	0.56	0.27		0.66	0.26	0.27	0.20
SO ₂		0.24				0.48	
NO		0.11					

Notes: The feed rate of all example compounds is 1 cm³/min, assuming sufficient oxygen for complete combustion is supplied. The listed p-ester compound is a phosphate ester employed in previous experiments on the destruction of hydraulic fluids for the DOE.

The relative humidity of the closed-loop system was maintained at a value of 50 to 60% at a temperature in the range 25 to 40 C (downstream of the PBR). This value was regulated by a cold heat exchanger/condenser (operated at about 7 C) and by adsorption in the dry soda lime CO₂ scrubber. In a large system using a wet scrubber, a heat exchanger/condenser (temperature of a few C) downstream of the scrubber would be adequate to regulate the humidity content to an acceptable level.

The CO level was allowed to rise up to a few hundred ppm in the closed-loop system, where it reached an equilibrium level. The CO level could have been further reduced by increasing the O₂ level above the maximum used (about 5%), but there was no strong reason for doing so. One of the strengths of the PBR is that it is not exactly a combustion device; hence, the O₂ level can have a much wider range than a combustion device such as an incinerator.

Gas samples were collected on adsorbent tubes for subsequent analysis. Two types of tubes were used: Tenax GR for the Malathion analysis and three-stage activated carbon for the MEK samples. Both of these traps were obtained from a commercial supplier (Supelco). The traps were chosen based on their ability to retain the target analytes over a reasonable sampling event. A sampling pump was used to draw the gas through the tubes, with sample times ranging from 5 to 10 minutes for most sample tubes. Flow rate through the sampling pump was 300 ml/min. Samples were collected for MEK in PBR-only (open-loop, closed loop), and combined PBR/SDP open-loop modes. Malathion samples were collected for combined operation of the PBR and SDP in open-loop mode only.

Standards were prepared in static dilution bulbs maintained in a laboratory oven. Standards were prepared from neat materials or from subsequent dilutions in purge and trap grade methanol. Heptane was used as the internal standard diluted from the neat material into a static dilution bulb.

Sample tubes were analyzed using thermal desorption/gas chromatography/mass spectrometry. The system consists of a 6016 thermal desorber autosampler (Tekmar) which sweeps the sample tube for 0.5 minutes and desorbs the tubes at 220 C for 5 minutes. This is transferred to a secondary analytical trap contained within a Tekmar 3000 purge and trap unit via a heated transfer line at 150 C. Sample gas is then collected on a Tenax trap. This trap is

desorbed at 200 C for 4.5 minutes. This sample effluent is transferred to the gas chromatograph via a second heated transfer line at 150 C which was connected directly to the analytical column. All valves within both systems were maintained at 150 C. After sampling, the purge-and-trap analytical trap was baked at 220 C for an additional 8 minutes.

The gas chromatograph (GC) was a Hewlett Packard 5890 equipped with a jet separator. Column flow was 10 ml/min, as measured at the transfer line to the purge-and-trap system. Samples were analyzed on a 30 m x 0.53 mm id x 3.0 μ m film thickness DB-5 column (J&W Scientific, Folsom CA). The initial GC temperature program was 40 C for 4 minutes, ramping at 14 C/min to 160 C. The jet separator and the transfer line were maintained at 220 C.

The mass spectrometer (MS) was a Hewlett Packard 5970 running in both scan and selected ion-monitoring mode. The scan mode measured from 40 m/z to 350 m/z with a scan rate of 3 scans per second. The electron multiplier was 1800 volts. Tuning was accomplished to maintain an ion ratio of approximately 30% for ions 131 and 219 while using perfluorotributyl amine. The selected ion monitoring mode used identical analytical conditions except that only ions 71, 126 and 127 were identified in the samples.

Sufficient time and project resources were not available to fully develop and qualify the rigorous sampling and analysis techniques demanded by such experiments. However, we are able to report preliminary results, within the limits imposed by the analytical techniques and the number of experimental runs carried out. The DRE is defined by the equation

$$\text{DRE (\%)} = (1 - [X]_{\text{out}}/[X]_{\text{in}}) \cdot 100 ,$$

where $[X]_{\text{in}}$ and $[X]_{\text{out}}$ are the respective influent and effluent concentrations. Table 2 shows our experimental DRE values for MEK and Malathion, calculated from the measured sample concentrations and the test-compound and carrier-gas feed rates. There was considerable spread in the data because of the degree of refinement of our analytical technique.

A tentative identification of byproduct compounds was done for the scan-mode samples analyzed. The most prominent of these compounds was benzene as identified by a match against a Wiley library search algorithm. Other compounds were found in the selected-ion mode samples but they could not be identified.

Table 2

Preliminary destruction results, in % DRE, for MEK and Malathion.

Configuration	MEK	Malathion
PBR only	99.998783 - 99.999983	99.998780 - 99.999642
PBR closed-loop	99.999947	- - -
PBR/SDP open-loop	99.999989	99.996423 - 99.999902

System Design Implications for Secondary Waste Generation and Handling

The components included in this closed-loop design for reaction-product partitioning include a heat exchanger/condenser, a dry soda-lime scrubber, and both bag and bed-type filters. Generally, the condenser is used to capture water so that it does not condense in the rest of the system. The dry soda-lime scrubber removes carbon dioxide and any acid gases present (it also adsorbs water vapor to some degree). The bag filter removes solid reaction products in such a manner that the system pressure drop is kept constant. The bed-type filter is a precautionary measure to remove fine particles before the gas flow is returned to the oxygen injection location (reduces oxygen reaction safety issues) and the PBR.

With any waste stream, mass is conserved. The difficult part of waste disposal is to decide what final forms are most manageable or desirable. When disposing of highly toxic materials, residuals and byproducts complicate or potentially contaminate the final form (this is a potentially serious problem for demilitarization techniques such as chemical neutralization). For a thermal system, when the waste contains only carbon, hydrogen, and oxygen the final forms are usually carbon dioxide and water. For a closed-loop system, a removal technique is needed. For the current configuration, CO₂ is removed by conversion to calcium carbonate in a bed of soda lime. The water is removed by condensation by a heat exchanger or is adsorbed in the soda-lime bed. Many other removal processes are possible and could easily be explored with the system we have developed.

When the waste stream contains chloride or fluoride, acids are usually produced. These are generally removed by a scrubber. In this case, the scrubber is soda lime and the final forms are calcium chloride and calcium fluoride solids that are left in the dry scrubber bed.

When the waste stream contains sulfur and phosphorus, the final form can be more complicated. The preferred form for phosphorus is as P_2O_5 which is a solid that can be easily removed by a bag filter. If the water content is high enough to be condensed, some of the phosphorus will also be captured as phosphoric acid - a fairly viscous (similar to honey) material.

Generally, we prefer to filter out the P_2O_5 before condensation or adsorption of water. The handling of sulfur-based compounds is another issue. Generally, the sulfur ends up as elemental sulfur that is filtered or as a gas such as SO_2 that is removed by the scrubber or SDP stage. The effectiveness of the soda lime in removing SO_2 has not been studied. A wet scrubber using sodium hydroxide is the most common technique for removing sulfur and also nitrogen compounds.

Chemical-Process Modeling

To establish a capability for using a chemical-process model to describe the operation of the PBR/SDP system, computer-based calculations using the commercial chemical process simulator AspenPlus¹⁰ were carried out. Because sufficient thermochemical data for Malathion were not available, the simulations were restricted to MEK. The baseline process flow diagram used in these simulations is shown in Figure 9. The recycle connection is employed only for closed-loop emulation. The PBR is a unit operation for which neither the kinetics or stoichiometry are well known at this time, because of the complexity of the cracking and oxidation reactions which occur within the vessel. Thus the PBR was simulated by a reactor option for which the user specifies a yield for the various product components. The yield distribution specified was based on the measured concentrations at the exit of the packed bed. The effects of varying that yield distribution will be explored. Since carbon (namely soot) is a product of the PBR, a means of simulating deposition of carbon is required. The standard reaction option (with specified yield) cannot accomplish this alone, thus we have added a separator unit (labeled RM-SOOT) at the exit of the PBR. The unit RM-SOOT simply strips all carbon out of the stream and places it in the output stream labeled SOOT1. It is understood that the flow rate in SOOT1 is the estimated carbon-deposition rate in the PBR. If the stoichiometry and kinetic parameters were known for the combined pyrolysis, oxidation, and (possibly catalytic) reactions occurring in the PBR, several other reactor models are available in the Aspen code for including chemical kinetics.

The liquid-gas separator trap which follows the PBR is simulated using a single-stage flash drum (labeled TRAP1), which involves solving the vapor-liquid equilibria problem. The stream labeled LIQ1 on the process flow diagram gives the composition and rate at which liquid accumulates in the trap. The vapor leaving the trap is then sent to the SDP unit. The temperature of the flash drum can be varied easily during simulations to determine downstream effects. For the initial simulation runs, we have selected ideal solution/ideal gas physical properties options in solving the vapor-liquid equilibria problem. For runs with more realistic simulants such as Malathion, components such as phosphoric acid are likely to form. These will require modeling the resulting non-ideal liquid phase thermodynamics in order to accurately represent the vapor-liquid equilibria. Several models are available in the code for modeling non-ideal aqueous solutions.

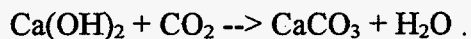
First-principle modeling of the SDP is beyond the present project scope. Thus, to simulate its role in the process flow diagram the simplification technique of free energy minimization was invoked. Although the SDP is a non-equilibrium process, determining the compositions predicted by free energy minimization does provide a useful bound - that of thermodynamic equilibrium. The unit operation selected for the simulation performs a Gibbs free energy minimization subject to atom balance, chemical reaction equilibria, and phase equilibrium constraints. It will also satisfy the charge balance constraint if ionic species are present. While chemical reactions can be specified, it does not require the user to specify the reaction stoichiometry (one need only list the possible product species). The module also has several options the user can control to mimic conditions where the system does not reach complete equilibrium. These include restricting the extent of a specified reaction (if the reactions are known), the fraction of a component that does not react, or the temperature approach to equilibrium.

Following the SDP reactor unit, the effluent passes through a filter bag designed to catch particulate matter (i.e. carbon). This unit is represented as a separator identical to that placed at the exit of the PBR unit. This unit simply removes the carbon from the SDP effluent stream and places it in the stream labeled SOOT2. The flow rate in SOOT2 gives the rate at which carbon (if present) would accumulate on the filter. As such, the filter action is perfect, i.e. all carbon is removed. This is easily relaxed to explore the effects of carbon on downstream operations since the fraction of carbon removed by the separator can be varied in the simulations.

The liquid-gas separator trap past the filter unit is simulated using a single-stage flash drum (labeled TRAP2). For the initial simulation runs, we have again selected ideal solution/ideal gas options in solving the vapor-liquid equilibria problem. The stream labeled

LIQ2 on the process flow diagram gives the composition and rate at which liquid (if present) accumulates in the second trap.

The off-gas from the filter is sent through an absorption unit designed to remove CO₂. The absorber is filled with Ca(OH)₂ which we assume reacts with the carbon dioxide according to



The charge also contains small amounts of NaOH and KOH, which we ignore for the present. For a first pass simulation, we treat the absorber as a reactor which follows the stoichiometry given by this reaction. For the baseline simulations, we specify that all CO₂ reacts with the hydroxide, i.e. the conversion of CO₂ is unity. This conversion can be relaxed (to less than unity) as a means of representing incomplete gas-solid contacting in the absorber. The code is not presently configured to rigorously handle a stationary bed of absorbent, thus we use a flow reactor option and simply flow excess quantities of hydroxide through the reactor. The unreacted hydroxide and the carbonate product are then removed from the effluent stream using a separator block. The composition of this effluent stream labeled I3 gives the rate of conversion to carbonate, which can be used as a first order estimate of the lifetime of a hydroxide charge for given process flow rates.

The first process simulations were to use experimental feed rates of methyl ethyl ketone (MEK), argon, and oxygen, and calculate the composition of the PBR product if it had come to chemical equilibrium (as determined by free energy minimization). In both cases (20% O₂ in Ar, 5% O₂ in Ar) the equilibrium product was calculated to be entirely composed of carbon dioxide and water. This outcome resulted from the oxygen flow rate being far in excess of that needed to completely oxidize the MEK. Since the observed data did not match these values, this meant that the mixture reactor had not come to equilibrium in the PBR. The residence time of the MEK in the PBR was calculated to be approximately 0.4 seconds, significantly less than typical pyrolysis residence times. This could account for the mixture not reaching equilibrium.

The next set of simulations used the flow sheet described above with a PBR yield distribution chosen to match the experimentally observed quantities of CO, CO₂, H₂O, and MEK. Several downstream observations are worthy of discussion. First, no liquids were captured in either trap. Second, the discharge from the SDP unit contained only CO₂ and water. This free energy minimization result is consistent with the excess of oxygen present in the feed stream. In anticipation of the formation of hydrocarbons in the PBR, simulations were also conducted wherein likely quantities of various hydrocarbons (up through C₆H₆)

were added to the flow between the PBR and SDP units. Again, it was found that the hydrocarbons were all converted to carbon dioxide and water during free energy minimization calculations in the SDP. Additional measurements of the SDP discharge are necessary in order to determine how best to constrain the equilibrium calculations in the SDP unit to match experimentally observed concentrations.

In subsequent simulations aimed at determining process sensitivity, less than total destruction of MEK was allowed in the SDP reactor and the impact of adding a recycle stream was explored. We specified that only 99% of the MEK could reach equilibrium in the SDP free energy minimization calculations (the remaining 1% passes through unreacted). Without recycle, this unreacted MEK would simply be sent to the vent. A recycle stream was introduced as shown in Figure 9. We then varied the fraction of stream I5 which was returned to the PBR feed stream as a recycle. Figure 10 shows the MEK concentration at the inlet to the SDP reactor (labeled SDPFD) and in the vent stream (labeled MEKOUT), as a function of the recycle fraction. In terms of the amount of unreacted MEK sent to vent, the beneficial effect of adding the recycle loop is clear. In these calculations, it was assumed that the product yield distribution (i.e. relative amounts of various products) remained unchanged in the PBR unit when the recycle flow rate was varied. With more refined knowledge of the PBR yield distributions and extent of destruction in SDP reactor, a more confident process analysis and optimization could be conducted. Also, the exploration of other process flow diagram topologies could readily be explored (e.g. placing the recycle stream just around the SDP reactor).

Summary

A technical basis for applying a Los Alamos-developed advanced oxidation process to chemical warfare agent demilitarization has been established through the construction of two-stage apparatus, initial chemical decomposition experiments, and process modeling. A major accomplishment has been to operate the first-stage apparatus under stable closed-loop conditions, thereby demonstrating the technical feasibility of closed-loop operation.

Publications

No publications related to this effort have yet been produced. We expect that at least one paper on this work will be completed at a later date.

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Figures (see enclosed illustrations and photographs)

Figure Captions

Figure 1: Schematic diagram of two-stage packed-bed reactor (PBR) - nonthermal plasma reactor (NTP) concept.

Figure 2: Schematic diagram of experimental apparatus, as configured for open-loop tests.

Figure 3: Schematic diagram of experimental apparatus, as configured for closed-loop tests.

Figure 4: Photograph of two-stage PBR/SDP apparatus constructed for this project.

Figure 5: Photograph showing detailed view of the PBR stage.

Figure 6: Schematic diagram of a single dielectric-barrier reactor.

Figure 7: Photograph showing a detailed view of the SDP-reactor stage and housing tank.

Figure 8: Chemical-structure diagrams of nerve agents and representative simulants.

Figure 9: Process flow diagram for chemical-process simulations (the recycle connection is used for closed-loop emulation).

Figure 10: Results of recycle calculations for MEK processing.

Advanced Oxidation Technology for Chemical Demilitarization

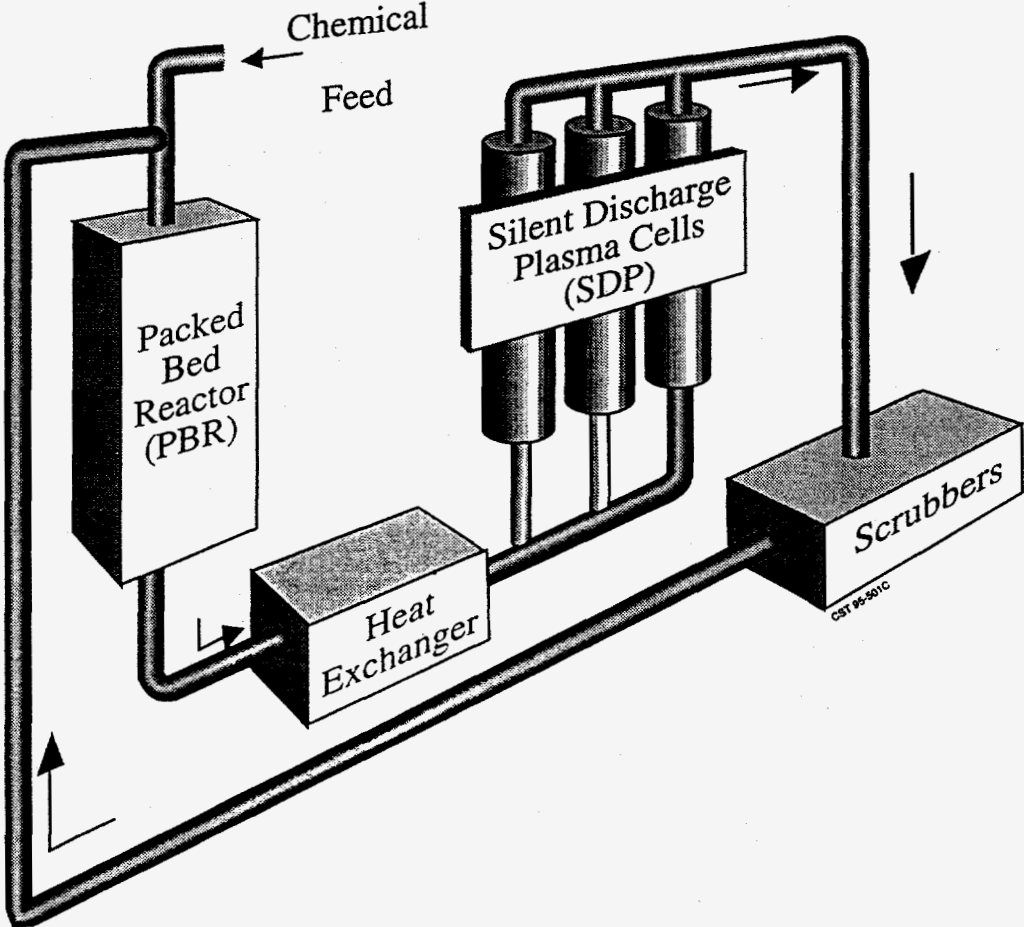


Figure 1

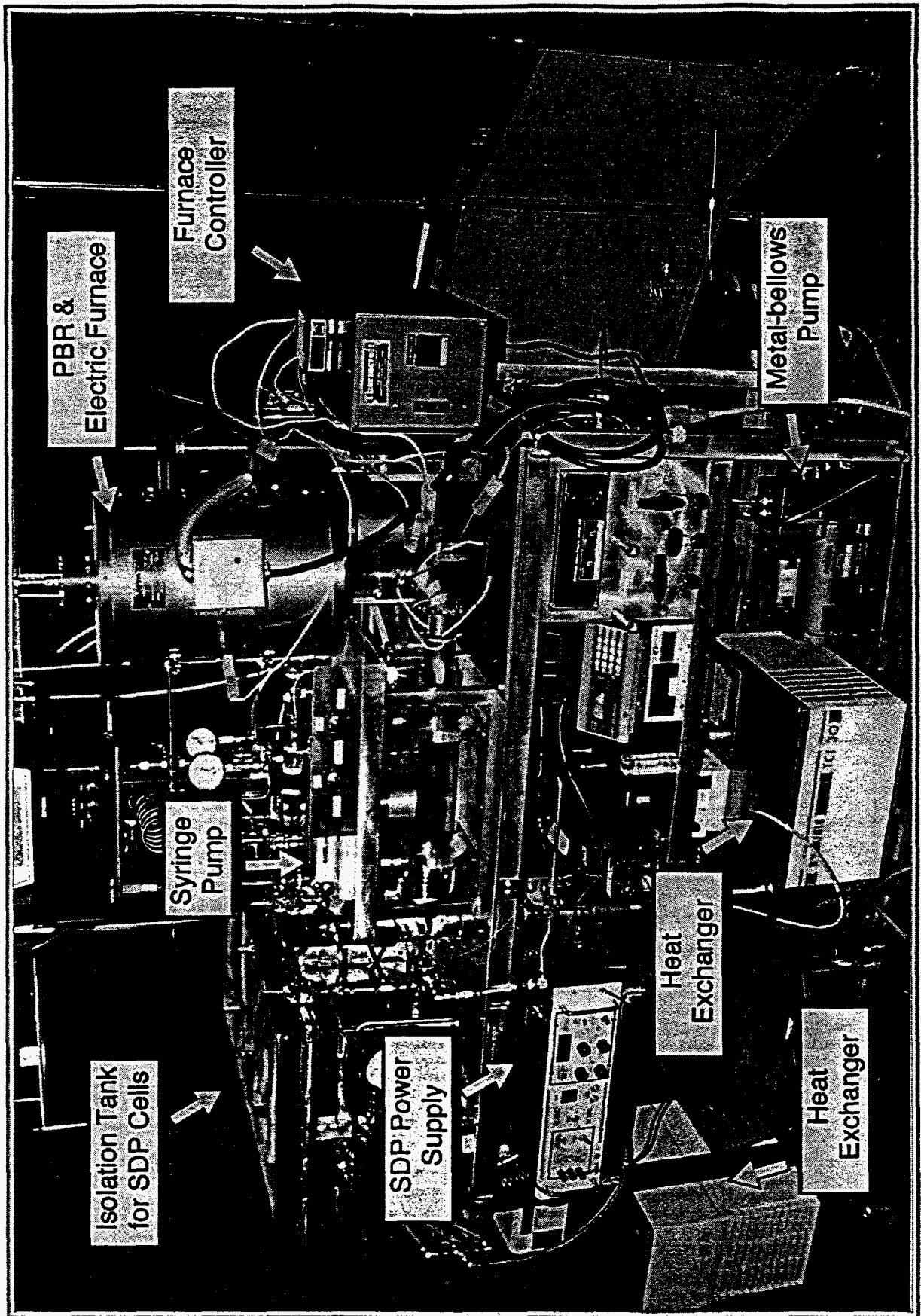


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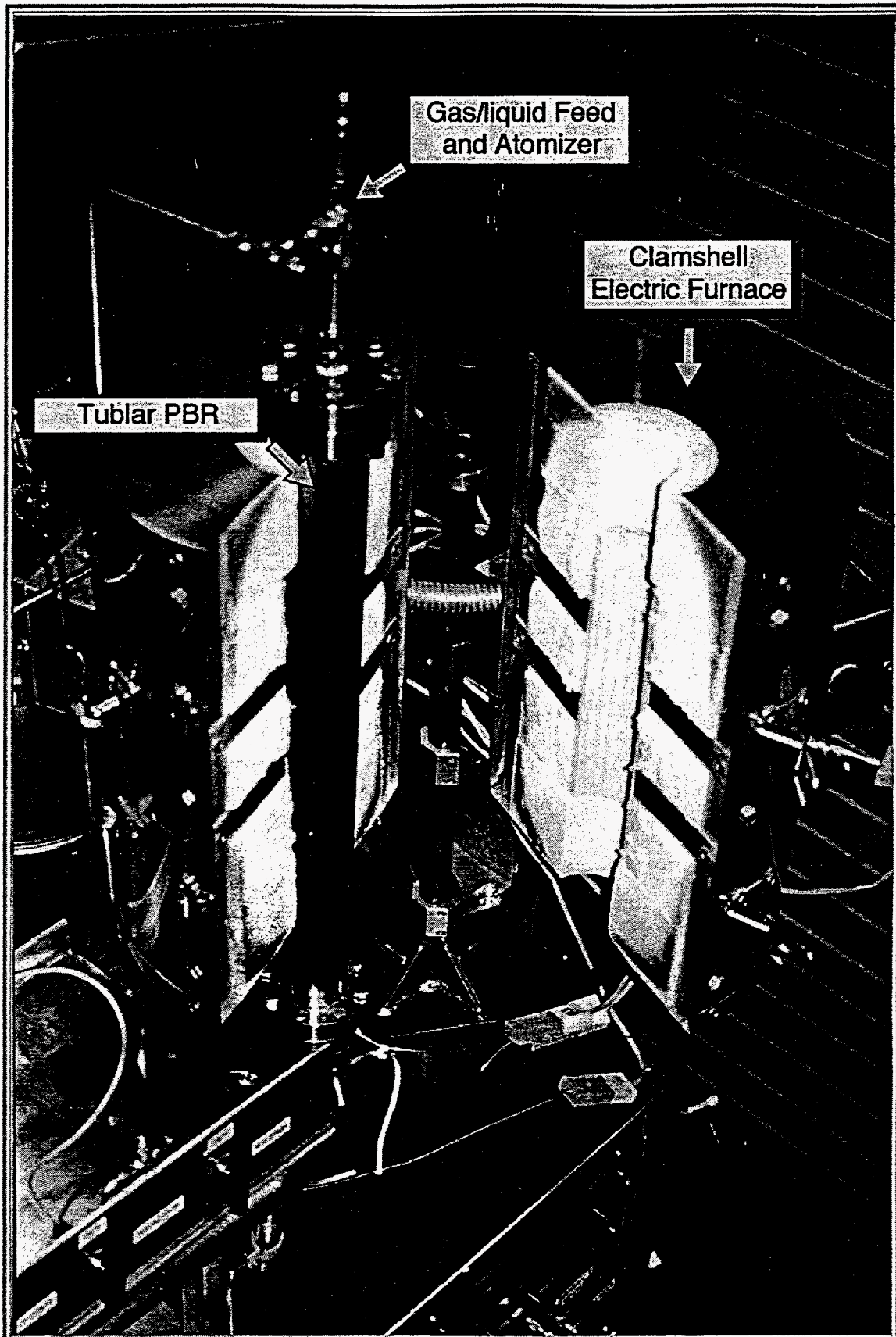


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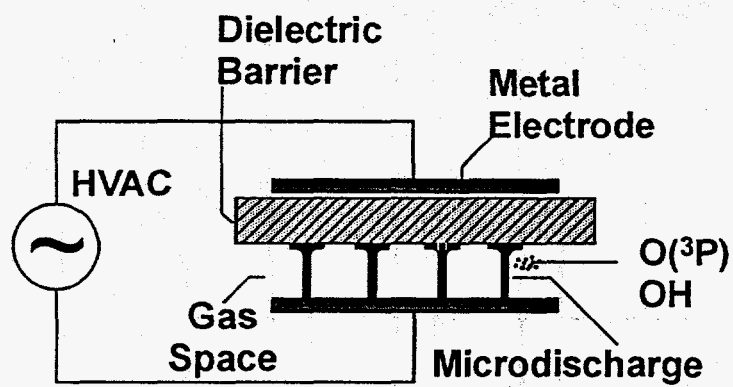


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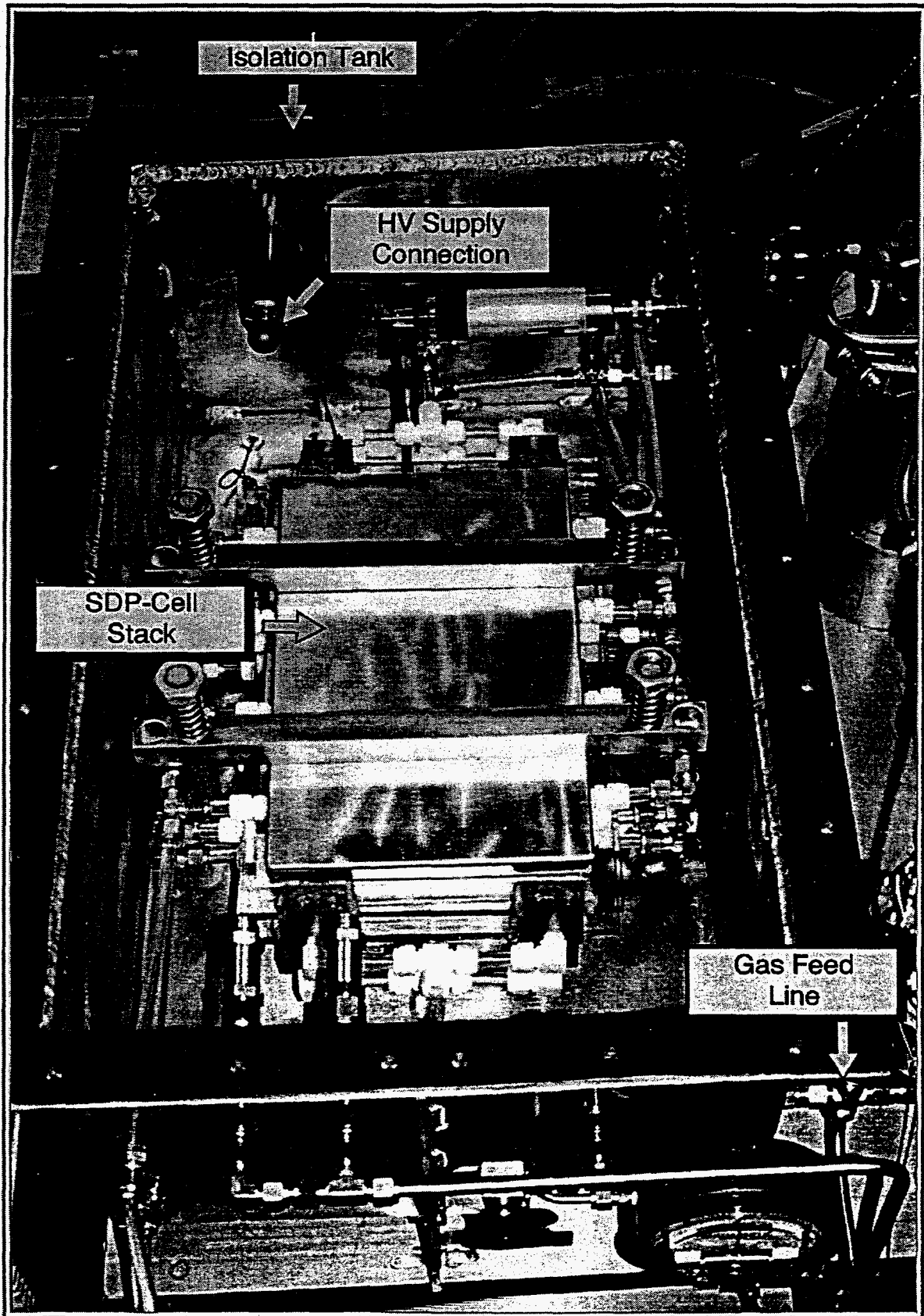
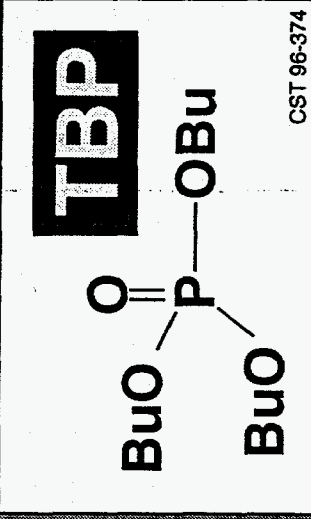
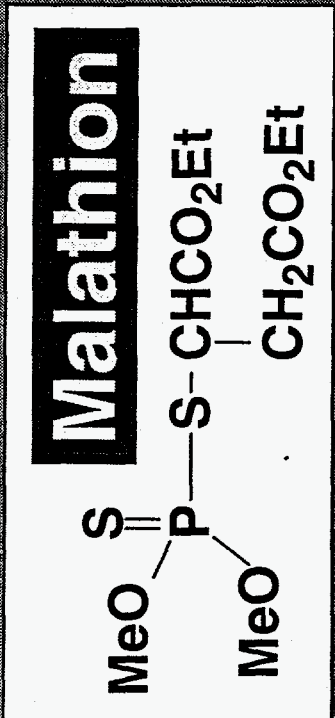
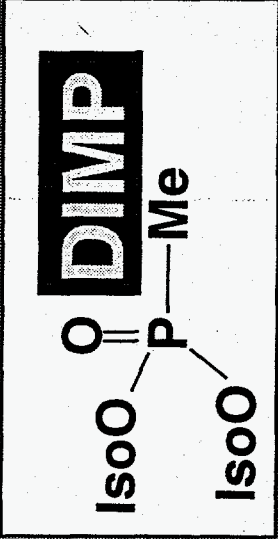
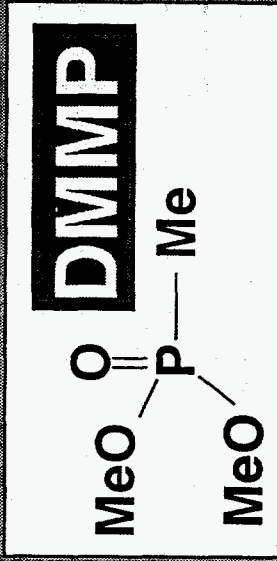
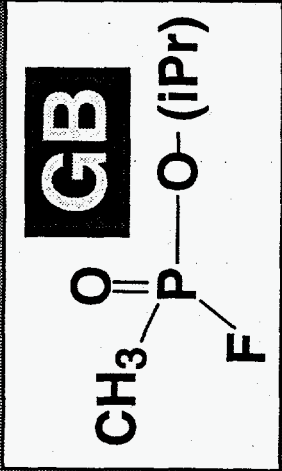


Figure 7



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Figure 8

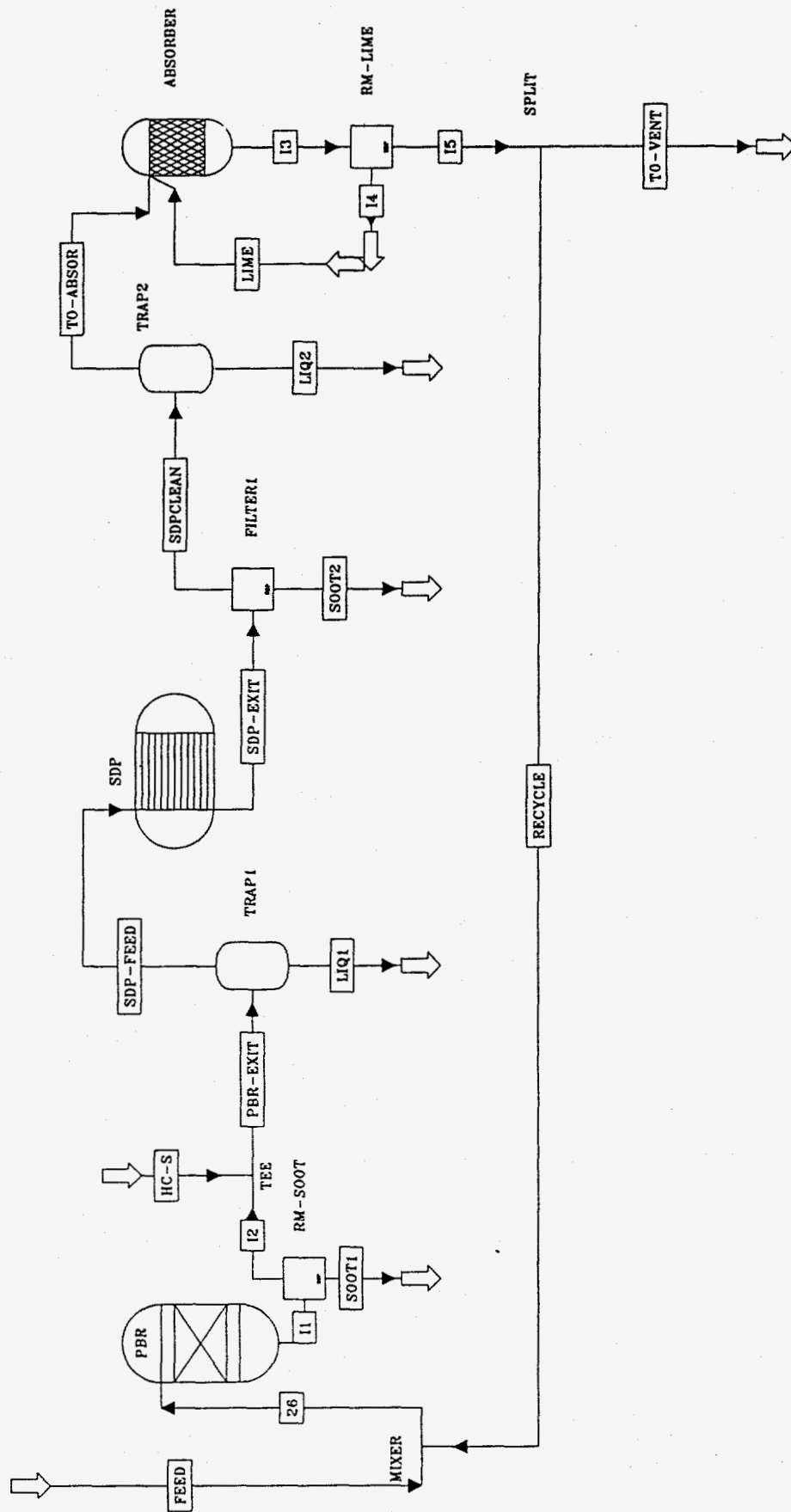


Figure 9

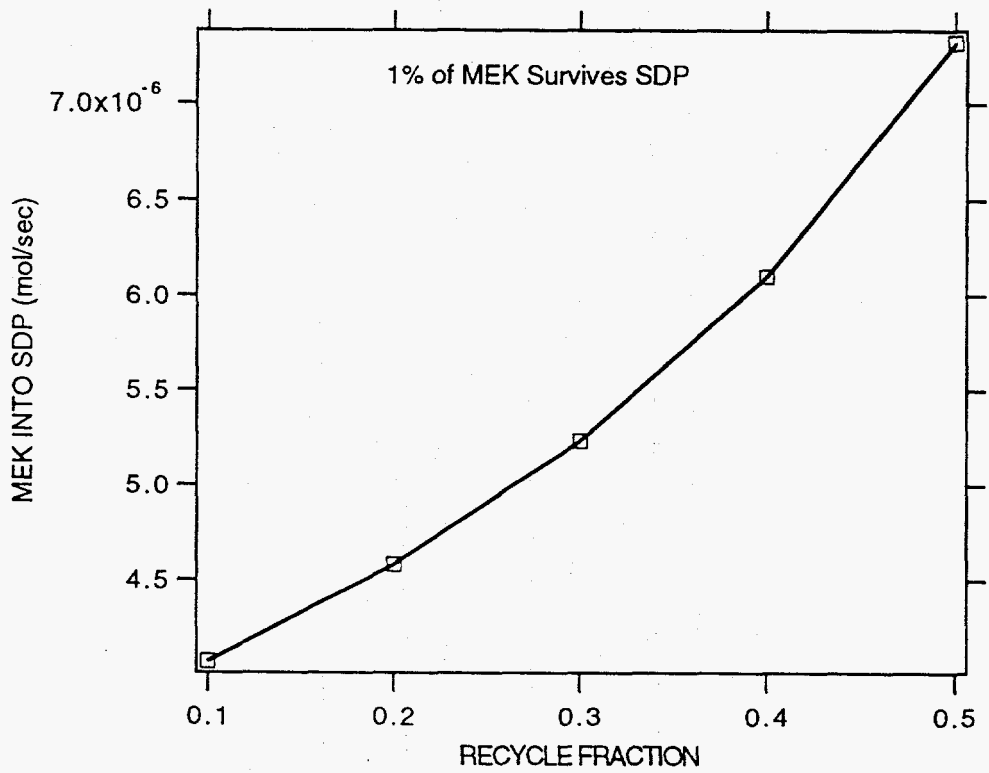
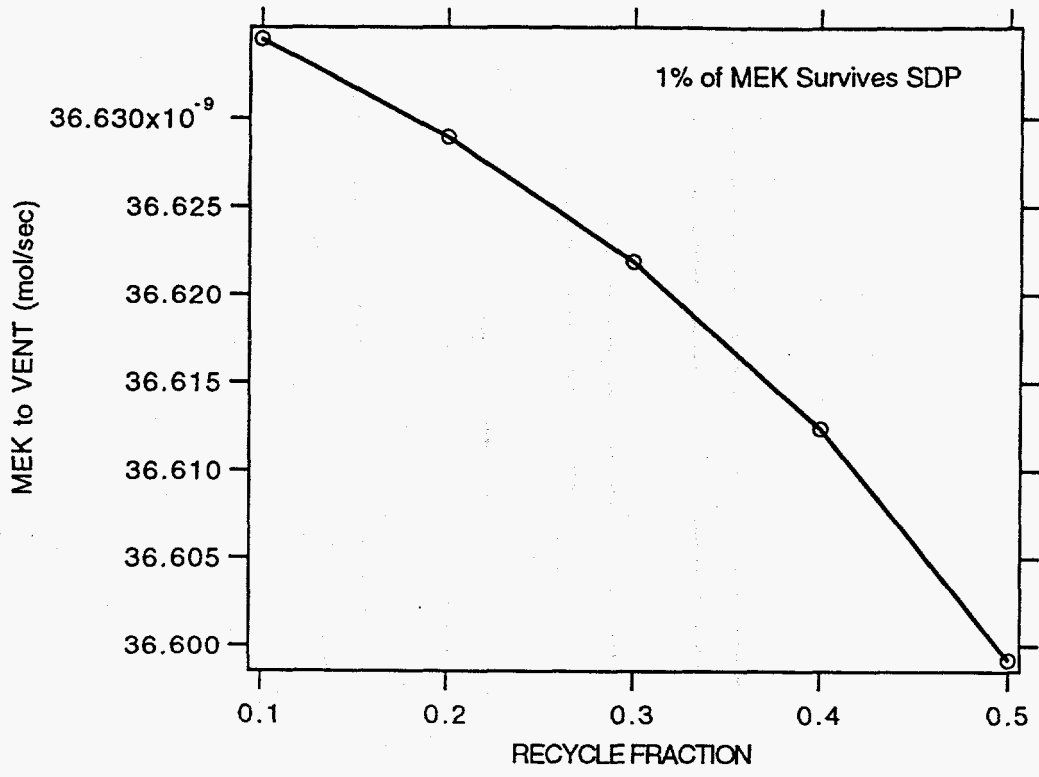


Figure 10