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Project Summary

Potential Technologies for Collection and Destruction of CFCs, Halons, and Related Compounds

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This report gives recommendations of a multidisciplinary panel of experts on new or novel technologies (or modifications of existing technologies) which show the most promise for the collection and destruction of chlorofluorocarbons (CFCs) and related compounds. The panel members met in a "roundtable" format to discuss their experiences and relate them to the compounds of interest. The panel identified technologies that held the most promise and suggested general areas of research and development needed to develop collection and destruction technologies.

This Project Summary was developed by EPA's Air and Energy Engineering Research Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

A family of chemicals known as chlorofluorocarbons (CFCs) has been implicated in the depletion of stratospheric ozone. A number of adverse health and ecological effects could result from such depletion. For this reason a number of strategies or options for controlling the release of these compounds are being evaluated by governments and industry worldwide.

Existing technological means have not been conclusively demonstrated as suitable for curtailing CFC emissions from certain sources to acceptable levels. Because of their great chemical stability, CFCs are very difficult to break down. In order to be destroyed, the CFC would first have to be collected. Thus, EPA felt a program was needed to evaluate various existing and new or novel technologies for the collection and destruction of CFCs.

The Navy needs new or novel technology to remove and destroy toxic compounds which may be used in chemical warfare (CW) The current generation of shipboard CW defensive systems are based on activated carbon adsorption. These devices are considered effective against high molecular weight, low volatility chemicals such as "nerve agents" which are strongly adsorbed. However, in order to deal with high volatility, weakly adsorbed toxic compounds (such as hydrogen cyanide, HCN), a reactive impregnant has been added to the carbon. It is known that some CFCs are not strongly held on carbon, so it was assumed that (if a technology could be developed for collection and/or destruction of CFCs) it might be possible to modify such a process for shipboard use as a CW defensive system.

To this end, the U.S. EPA and the Navy proposed assembling a multidisciplinary panel of experts to recommend new or novel technologies (or modifications of existing technologies) which show the most promise for future development. The panel would then meet in a "roundtable" format to discuss the proposed technologies. This report gives results of this meeting.

Summary of Expert Panel

To address the issues for the EPA and the Navy in terms of their particular interests, the technologies were evaluated for two distinct classes:

- Technologies capable of collecting, removing, or destroying the compounds from the feed stream and providing an off-gas or effluent suitable for breathing air (for example, shipboard CW defense); and
- Technologies capable of collecting, removing, or destroying the compounds from the feed stream with no requirement for a breathable off-gas (for example, bulk incineration of contaminated CFCs).

The panel reviewed many technologies including thermal, chemical, and biological processes. In most instances biological processes can be used only on dilute aqueous streams and the biological destruction rate is very slow. This is based on experience with highly halogenated polychlorinated biphenyls (PCBs). Therefore, for the two applications at hand, biological processes were eliminated as possible candidates.

The overall conclusions of the expert panel for the breathable air situation was that the use of carbon adsorption as currently done by the Navy was the most reasonable, commercially available process. However, carbon adsorption is limited because high volatility toxic compounds are not strongly held on carbon, and the reactive impregnants which are added to remove these compounds are non-specific (they react with a host of other contaminants) and of limited capacity. Furthermore, there is currently no method to determine when the carbon needs to be replaced.

The potential candidates to replace the present carbon adsorption system are:

- Inorganic Membranes: These may be either ceramic membranes or carbon molecular sieves. Inorganic membranes operate at high temperatures and are chemically resistant. A carbon bed may still be required downstream or metallic salt impregnants may be needed to react with high volatility compounds.
- Chemical Scrubbing/Destruction: This technology includes the use of a highly alkaline, non-aqueous scrubbing liquor to absorb and destroy the compounds of interest. This is superior to scrubbing alone, since equilibrium limitation is removed. Downstream treatment is required to prevent contamination of the carbon bed. Pretreatment of the inlet air may be required to remove moisture.
- Corona Discharge: This process uses highly energized electrons from an ionized corona discharge to dissociate the compounds of interest. This process operates at essentially ambient temperature and pressure. A carbon bed may still be required downstream. A high voltage power supply is required and ozone and/or NO_x may be generated.
- Metals Scrubbing: This technology uses an active metal such as zinc or aluminum to react with the compounds of interest. It is known that active metals can rapidly destroy halogenated organics such as PCBs. One advantage is that a solid salt may be formed which can easily be removed. Pretreatment of the inlet air may be required to remove moisture since there may be a problem in maintaining an active metal surface in the presence of air and moisture.
- New Adsorbents: This technology uses tailor-made adsorbents, such as new zeolites, and aluminas, or polymeric adsorbents, to obtain the desired separation. These compounds have a uniform or well-defined structure which results in more consistent performance. Also, their properties may be altered using various pretreatments. A new selective adsorbent bed could conceivably allow some less toxic compounds through to be handled by a cheap carbon bed instead of an expensive specialty adsorbent bed.

In the area of destruction of fully halogenated organics without the need of a breathable off-gas, current thermal destruction processes may be adequate. CFC wastes are currently being destroyed in at least one permitted facility. The harsh environment created by the hydrogen fluoride (HF) in the off-gas is one potential cause for concern; specially designed internal firebrick and mortars may be required.

Although CFCs are currently b incinerated, there are very limited regarding the destruction efficienc products of incomplete combus (PICs) resulting from these operati Data are lacking regarding the qua and fate of PICs; such compounds be toxic and/or may pose a threa stratospheric ozone.

To summarize the status incineration of CFCs, this is the demonstrated technology whicl currently being used, and will li continue to be used in the near t However, the feared potential of corr attack to the refractory and the lac accurate data on destruction effici and PICs are problems which re solutions.

Other technologies which recommended as good candidates w there is not a need for breathable air

- Catalytic Thermal Destruc Metal catalysts have b successfully used to destroy hydrocarbon gas stream reduced temperature, the saving energy and improving economics of this co technology. Potential problems the destruction of chlorir hydrocarbons using this techn include low destruction effic due to catalyst deactivation.
- Chemical Scrubbing/Destru This process has already described for breathable air.
- Corona Discharge: This pr has already been describe breathable air.
- Metals Scrubbing: This proces already been describec breathable air.
- Pyrolysis: This technology in thermal treatment in the absei air. Since CFCs are dest through bond homolysi hydrolysis, simple heating w air is sufficient to break the b Heating without air resu reduced gas flow which can smaller downstream trea equipment. Potential prol include the possibility of co attack and the formation of amounts of PICs.
- Supercritical Water Oxic (SCWO): This is a modifica Wet Air Oxidation (WAO scribed below) which invo supercritical fluid (water). Th technology features much reaction rates than those ach

in the well-known WAO technology. Furthermore, SCWO operates at very high oxidant concentrations which enhance the kinetics and produce favorable equilibria. Potential problems are greater energy requirements and possible metallurgical limitations.

- Wet Air Oxidation (WAO): This process uses a high temperature (>300°C) aqueous stream and oxygen to destroy many organic compounds. Since CFCs do not contain a hydrogen atom or a double bond, they are expected to be resistant to oxidation. However, CFCs are susceptible to hydrolysis during incineration, so a high temperature aqueous treatment could be effective.

Recommendations of the Expert Panel

The expert panel agreed that several areas deserve priority for further research.

CW Defensive Systems (Breathable Air)

- The panel agreed that future research in this area should begin with fundamentals in order to determine the optimum long-term solution.
- The corona discharge process and the ceramic membrane process were proposed as good potential candidates for initial research.
- Liquid scrubbing with a reactive component may have application; however, the Navy is concerned with high humidity in the breathable air.

CFC Destruction (Non-Breathable Air)

- A literature search is needed to assemble all available data on previous experience with conventional thermal oxidation (incineration) of CFCs.
- Products of incomplete destruction (PICs) should be identified for residual ozone depletion potential and toxicity In particular, the formation of F and Br analogs of dioxin should be investigated. Also, the thermal stability of CFCs and their basic combustion properties should be studied
- Inorganic membranes should be studied from a materials science perspective. Also, new adsorbents should be investigated.
- The chemistry of scrubbing systems which contain a reactive component should be studied.
- The corona discharge process as it currently exists requires small scale tests, energy efficiency measurements, and modeling.
- Refractory linings that are resistant to HF should be studied and tested.
- Potential catalytic materials for catalytic thermal destruction should be evaluated.

Conclusions

The expert panel discussions on the most favorable technologies that warrant future development for CFC destruction and naval CW defense lead to the following conclusions.

1. There do not appear to be any new near-term technologies which are as capable as activated carbon in removing a broad spectrum of toxic CW agents from shipboard air.
2. Longer-term options such as the corona discharge process and the ceramic membrane process should be pursued as research projects where these options could lead to improved technologies for shipboard CW defense compared to conventional carbon adsorbers.
3. Thermal incineration appears to be feasible in the near-term for the destruction of bulk quantities of CFCs (such as contaminated refrigerants or waste solvents), although materials of construction for the incinerator and byproducts of combustion should be further researched.
4. Sources of dilute emissions of CFCs may require technologies available in the longer-term. These options, which include technologies such as catalytic thermal destruction, pyrolysis, or wet air oxidation, may be source-specific.

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The complete report, entitled "Potential Technologies for Collection and Destruction of CFCs, Halons, and Related Compounds," (Order No. PB 89-219 968/AS; Cost: $15.95 subject to change) will be available only from:
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