CATALYTIC OXIDATION FOR COLLECTIVE PROTECTION

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ABSTRACT

Collective protection with a self-decontaminating filtration system increases the warfighter's effectiveness and decreases the logistics burden. The CATOX/PTF (catalytic oxidation/post-treatment filtration) system destroys greater than 99.9999% of agents with only carbon dioxide and water as products for multiple attacks without maintenance. A 1994 study estimated that CATOX/PTF has 10 times less cost during a 1-year wartime period compared to traditional carbon filters. Since then, the catalyst activity and PTF capacity has been increased by 15 times. The CATOX operating temperature and residence time are sufficient to sterilize biological agents, which reduces the required particle filtration efficiency. Recent analysis and testing indicates that CATOX/PTF offers better protection against TIC/TIMs. Benefits occur when the CATOX/PTF is integrated with an ECS (environmental control system). To illustrate, examples of ECS/CATOX/PTF subsystems will be provided for a new generation of armored vehicles, an existing cargo aircraft, and a shelter concept.

INTRODUCTION

Platforms that rely on individual protection may limit the warfighter's effectiveness. Although chemical agents are removed from the air supply stream, there is no purified air that can be supplied to the cabin/crew compartment or cargo hold for pressurization or to the electronics/avionics bay for cooling (Fig.1A). The contamination of these areas represents a major vulnerability. During a mission, NBC agents in the cabin or leaking from the bays or hold are threats to the crew through contact with skin. Further, the corrosive nature of chemical agents and pose a threat to the electronic equipment. After a mission, the interior of the plane or vehicle must be decontaminated, threatening the platform's survivability.

In addition to purifying the breathing air, collective protection provides a shirt-sleeve environment by overpressurizing the cabin or crew compartment with purified air, and providing purified air to the cargo area, and electronics/avionics bays. Thus, the filtration system needs to purify higher flowrates, but with low weight, small installation footprint, low pressure drop, low energy draw, and a high degree of integration with the environmental control system.

Under these limitations, non-regenerable filters may suffer from a heavy logistics burden. For example, if filters need to be replaces after a limited number of attacks, a supply train of additional filters must be available. Moreover, if the filters contain live agent, their disposal is hazardous, costly, and intensive. Regenerable filter systems reduce the logistics burden by periodically releasing their trapped inventory of live agent or partially destroyed agent, as opposed to changing filters. However, there is danger when releasing agent or in the event of a leak.

An ideal solution to these constraints is to apply *destructive* filtration (Figure 1B), in particular, catalytic oxidation. The concept is depicted in Figure 2. The catalytic oxidation reactor (CATOX) operates at moderate temperatures to catalytically oxidize greater than 99.9999% of chemical agents to carbon dioxide and water. Heteroatoms in the agents such as phosphorus, nitrogen, sulfur, or chloride turn into a much less toxic form than chemical agents and are removed with a post-treatment filter (PTF). There are no valves, seals, or moving parts to affect reliability. Biological agents are destroyed, which

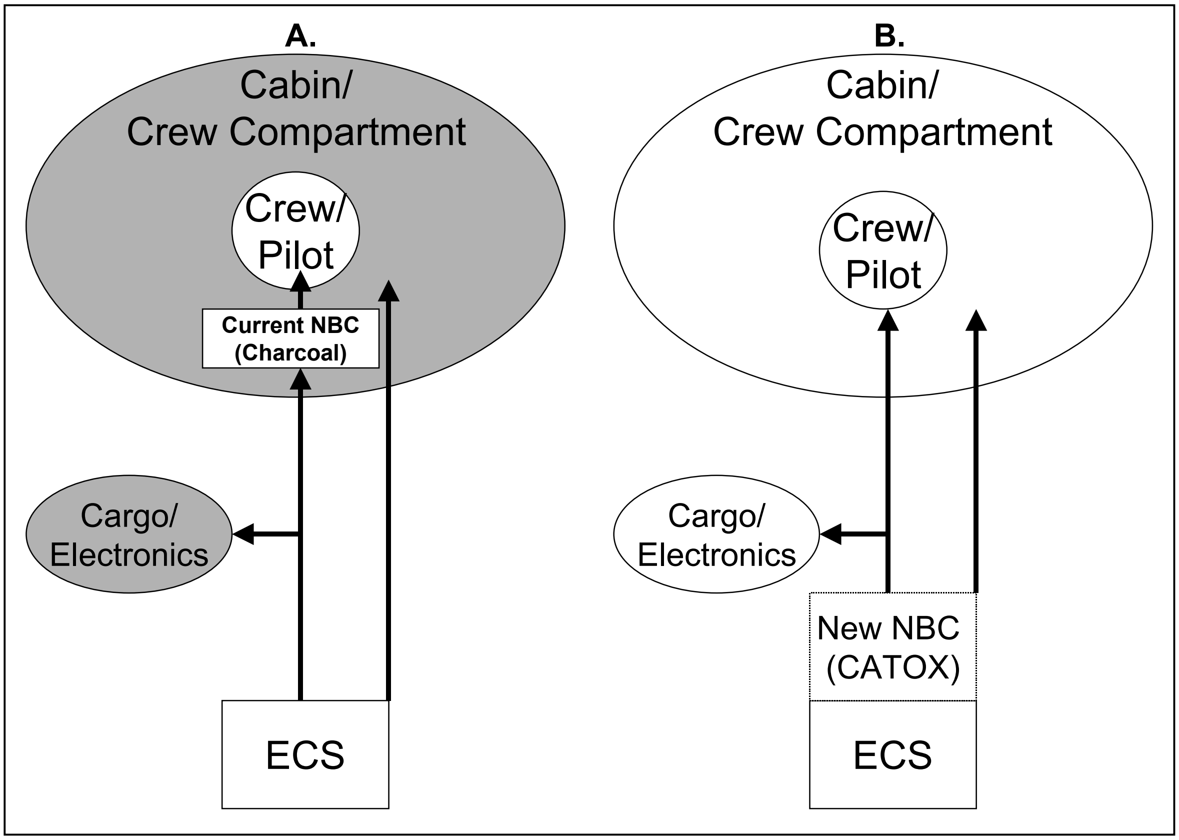

Figure 1. A) Current NBC filter is ideal for breathing air purification, but low capacity not suited for purifying air to overpressurize crew compartments, cargo holds, electronics bays (shaded areas); B) CATOX/PTF purifies air to all locations and for multiple attacks without maintenance.

means a high-efficiency particulate air (HEPA) filter may not be required. Thus, the CATOX/PTF system provides purified air to the environmental control system (ECS) for cooling.

CATOX is the heart of Honeywell's NBC system. The technology is well-understood and proven through 30 years of testing. The new integrated PTF combines with the CATOX to produce only carbon dioxide and water from the agent-laden stream. After a review of the technology and key programs, recent advances will be described including systems integration approaches with the ECS and Power Thermal Management System.

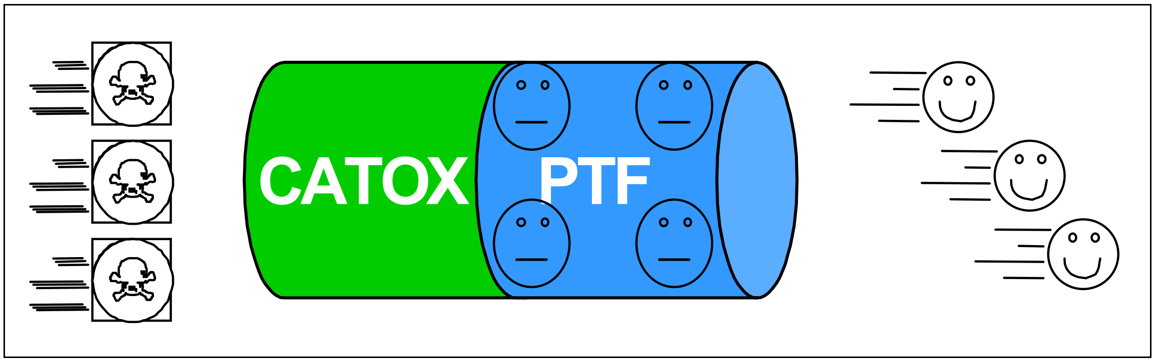

Figure 2. CATOX/PTF destroys Chem-Bio Agents and TIC/TIMs.

TECHNOLOGY OVERVIEW

Catalysts are key components in a large number of high technology industrial applications. They promote chemical reactions at significantly milder, more economical, and more practical conditions by lowering the activation energy required for the desired reaction. By definition, a catalyst is not physically or chemically altered as a result of a reaction. Catalysts are often composed of very stable, specialized materials, including noble metals like platinum.

The use of catalysts is widespread and essential to major industries. In fact, 90% of the processes used to make the $1.3 trillion of chemicals per year worldwide are catalyst-based[i]. As an example, essentially all gasoline is produced from petroleum using several high technology catalytic processes, such as reforming, alkylation, and cracking. Honeywell, through its UOP division, helped start the refining industry by developing one of the earliest processes, and later introduced the first industrial process using platinum catalysts in the late 1940s.

Another example is the automobile catalytic converter, which was pioneered by Honeywell in the 1960s. Virtually all cars sold in the U.S. and Japan since 1975 are equipped with a catalytic converter to convert unburned hydrocarbons, carbon monoxide, and nitric oxide to harmless compounds. Similar technology is used in the oxidation of chemical agents.

Examples of catalytic systems in commercial breathing applications include the removal of ozone by a catalytic converter from the outside atmosphere before delivery to the passenger cabin. Honeywell recently set an industry standard for converter efficiency and lifetime on the Boeing 777, and also supplies the converter for the Boeing 767-400ER, 757-300, and the Dornier 328JET.

Catalysts are included in the multi-step air purification process on the International Space Station, as well as many indoor air quality applications.

The widespread success of the above applications proves that many technical hurdles, such as maintaining high catalyst activities with long lifetimes, have been overcome. The following section describes the success of catalysts in key NBC programs.

TECHNOLOGY MATURITY

Honeywell System is the Most-Tested, Highest Performing CATOX for NBC

In military-funded programs since 1964, CATOX has demonstrated complete destruction of agents. Further, the Honeywell CATOX system is the only catalyst system to have accumulated thousands of hours of testing. The key programs are described below.

Medical Unit Self-contained Transportable (MUST) hospitals[ii]. A 400 cfm air conditioning unit was integrated with a CATOX collective protection system, which was challenged with GB over 82 hours. The three test rats survived breathing the output air. In separate tests, there were no surviving *Bacillus globigii* (Bg) spores.

Army-CRDEC program[iii] for catalyst development. Various catalyst formulations were tested for the destruction of agents GB, GD, VX, AC, HD, Lewisite, and the simulant DMMP with abnormally high agent concentrations in humid air for 4,000 hours at 250°C. This was the first study to use monolithic catalysts instead of packed beds. Monolithic catalysts have advantages of higher destruction efficiencies at a given pressure drop, elimination of bed channeling, and more efficient catalyst utilization. The best catalyst formulation was chosen as the Military Air Purification (MAP) catalyst. The technology was a direct extension of Honeywell's pioneering automobile catalytic converters.

In the Chemical and Biological Air Purification System (CABAPS) program, the MAP catalyst was incorporated into a unit with a 20 lb/min flow capacity and tested with live agent against an Air Force threat scenario[iv]. The results were destruction efficiencies greater than 99.9999%.

For the Catalytic Air Purification System (CAPS),[v] Honeywell integrated a brassboard system of a CABAPS catalytic reactor with a refurbished, government-supplied M1A1 ECS, a PTF, and a HEPA filter. Testing at Dugway Proving Grounds under a threat defined by the U.S. Army Chemical School concluded that the CABAPS reactor was effective in destroying chemical agents.

The CATOX/ECU program's objective was to generate data to be used to design air purification systems for crew compartments of military armored vehicles, vans, shelters, and the like[vi]. The US Army successfully completed 240 hours of cyclic durability testing, including various shock and vibration loads. The catalyst was tested against chemical agents AC, GB, and GD over a wide range of operating conditions. The CATOX system maintainability and supportability was found to be ten times cost-effective compared to an existing baseline system (see Economics). The PTF was effective in removing sulfur and halogen heteroatoms, but not nitrogen.

Recent Activities Bring CATOX Closer to Deployment

Assessment of Technology for Assembled Chemical Weapons Demilitarization (ACWA) evaluated alternatives to incineration for destroying shells, rockets, etc. containing chemical agent[vii]. In one unit operation, CATOX was used with an alternative technology to protect against air emissions from potential failure modes. In another, CATOX achieved greater than 99.9999% destruction and removal efficiencies of GB, VX, and HD as the primary destruction technology, according to the National Research Council[viii]. The hundreds of hours of test experience on this program supported Undersecretary of Defense Aldridge's recent recommendation of that alternative technology.[ix] Subsequently, it was announced that the U.S. Defense Department has selected the same successful ACWA team, to design, build, operate, and close the Pueblo, Colorado Chemical Agent Destruction Plant[x].

The MAP catalyst has been incorporated into a Recirculating Air Purifier that destroys background levels of chemical and biological agents that may be brought into a shelter or room through the airlock. The advantages over the charcoal-based unit in the military inventory include longer life, higher efficiency, no release of removed agent, and destruction of biological agents. The DARPA-funded device, designed and built by MesoSystems Inc., is now undergoing advanced testing at SBCCOM Edgewood.

PURPOSE OF PRESENT PAPER

Since the CATOX/ECU program in 1994, Honeywell has continued its internal research and development program. Recent advances include:

- A new processing method for the MAP Catalyst that results in lower operating temperatures and smaller CATOX reactors for certain threat compounds
- A next-generation PTF that is highly effective for removal of nitrogen heteroatoms, as well as an order of magnitude increase in removal capacity for chloride heteroatoms
- The development of a TIC/TIM removal strategy.

Trade studies of systems using the improved components have been conducted on various platforms. This paper highlights these advances.

MAPlus CATALYST

A better processing method for the MAP Catalyst has resulted in improved performance. This version, called the "MAPlus" Catalyst, becomes active at lower temperatures than the original MAP Catalyst. For example, in Figure 3, diethyl sulfide is destroyed about 50°C lower than the original MAP. This breakthrough can reduce the CATOX energy requirement and start-up time. In some applications, the effect of certain heteroatoms on the MAP Catalyst must be considered when sizing CATOX. The MAPlus catalyst relieves that consideration. For example, for 48 attacks, the CATOX with the MAPlus catalyst is 4 to 15 times smaller than with the original MAP catalyst (Figure 4).

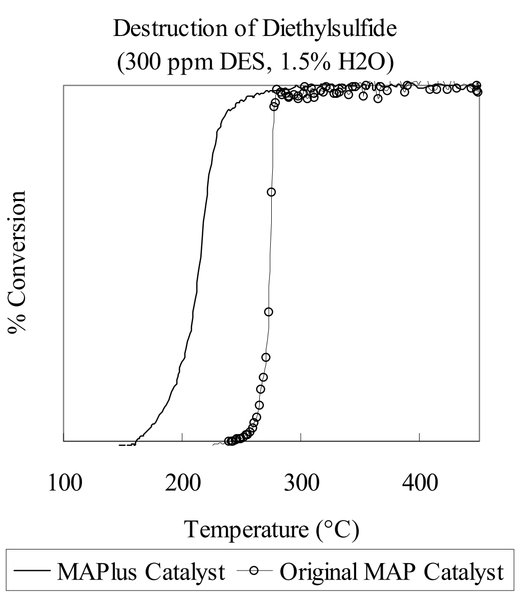

Figure 3. MAPlus Catalyst has destroys DES 50°C lower than original MAP Catalyst.

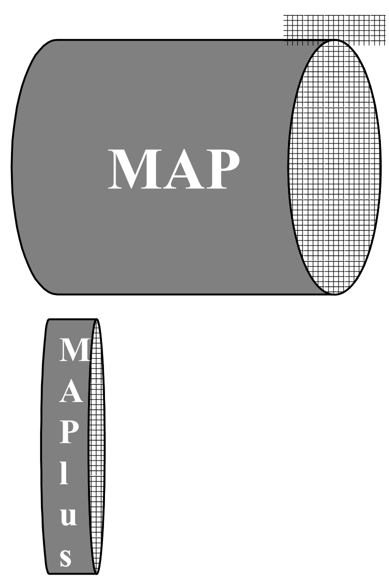

Figure 4. MAPlus Catalyst requires 4 to 15 times less reactor than original MAP Catalyst.

POST-TREATMENT FILTER (PTF)

Since the CATOX/ECU program, Honeywell's internal research has developed a series of next-generation PTFs with increased removal efficiency for nitrogen and chloride heteroatoms. Both are contained in cyanogen chloride (CK), which is often used as a design-limiting reagent because it is present in high concentrations in the Army threat scenario.

The first–generation of these patent-pending PTFs has the ability to remove the nitrogen heteroatom, which did not exist during the 1994 CATOX/ECU program. The second generation PTF has a 70% greater removal efficiency and is easier to integrate with the CATOX. Figure 5 illustrates the feasibility of the PTF approach for a shelter threat scenario. The integrated CATOX/PTF destroyed all of the triethylamine *without NOx* detected in the effluent for the equivalent of over 20 attacks. The only products are carbon dioxide and water.

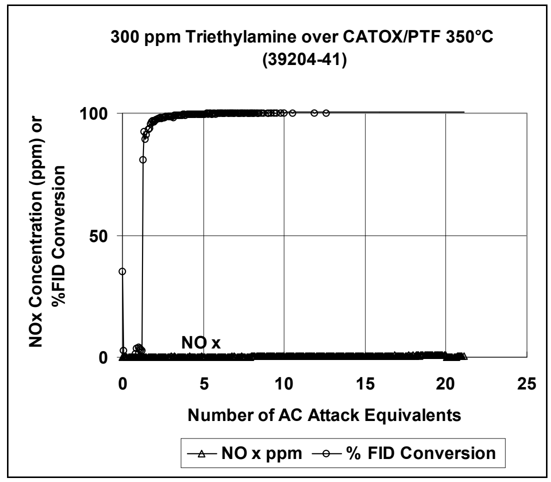

Figure 5. Complete destruction of 20 attacks without NOx byproducts.

The third generation PTF has further increased the efficiency for both nitrogen and chloride heteroatoms. Figure 6 shows that the capacity for nitrogen dioxide (NO_2) in a dry air stream at higher flowrates is an order of magnitude greater than that of the second generation PTF. Similar results are obtained for nitrogen oxide (NO). Performance in a humid stream is even better. Figure 7 shows that the HCl capacity has similarly been increased by up to 15 times compared to the original PTF used in the 1994 CATOX/ECU program.

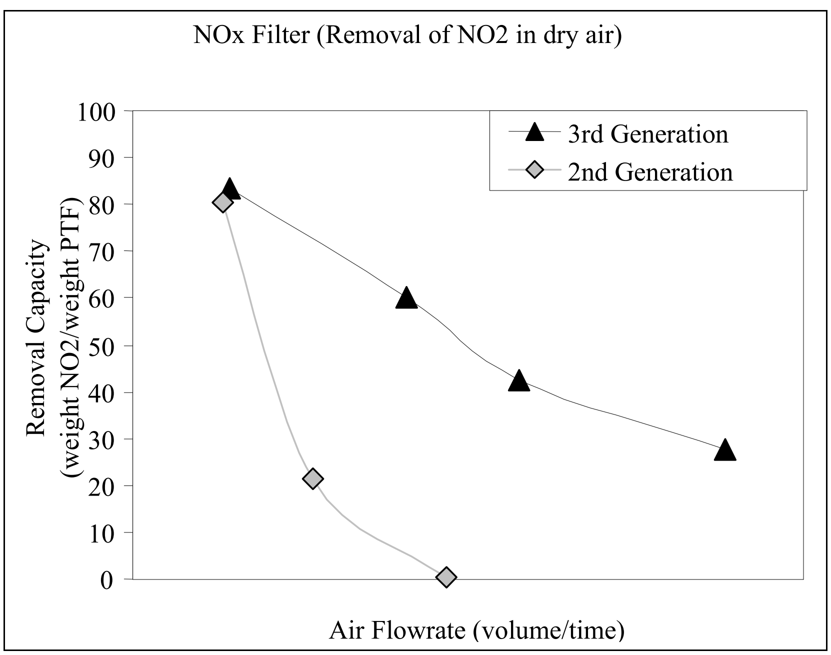

Figure 6. Third Generation PTF has order of magnitude greater NOx removal capacity.

These breakthroughs allow CATOX to provide pure air for multiple attacks with less weight and volume and no maintenance.

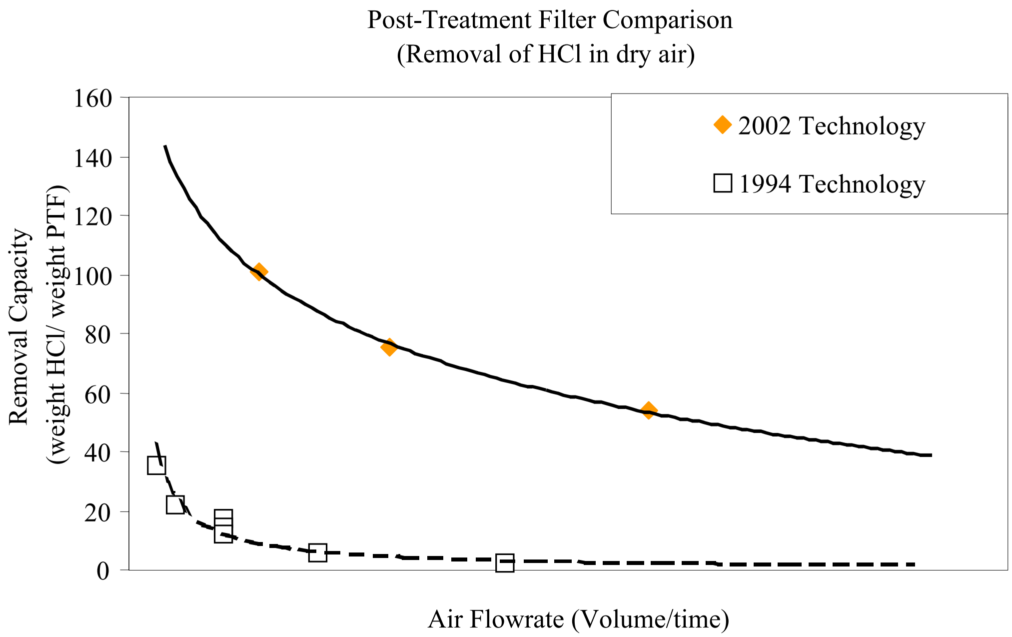

Figure 7. Third Generation PTF has up to 15 times higher chloride removal capacity.

TOXIC INDUSTRIAL COMPOUNDS / TOXIC INDUSTRIAL MATERIALS (TIC/TIMs)

Toxic Industrial Compounds/Toxic Industrial Materials (TIC/TIMs) are an emerging threat[xi]. Recently, the capability of the baseline carbon system against TIC/TIMs was assessed by the Army to be low[xii]. In contrast, limited data suggests that CATOX/PTF may have high capability against TIC/TIMs.

A combined ECS/CATOX system offers three primary modes of removal: 1) catalytic oxidation; 2) catalytic oxidation with removal of the heteroatoms by the PTF; and 3) removal by PTF. Typically, an integrated system will also include a water extraction system that can offer redundancy for the removal of water soluble TIC/TIMs. Generally, the primary destruction mode for organic TIC/TIMs will be the CATOX reactor. The CATOX will also oxidize inorganic TIC/TIMs, with the heteroatoms typically removed by the PTF. Existing literature and laboratory data indicates which will be primary destruction mode for the high and medium hazard index TIC/TIMs (Table 1). The other modes may also contribute to the removal of the TIC/TIM as well.

TABLE 1. TIC/TIMs sorted according to primary destruction mode

CATOX	CATOX/PTF	PTF
acrolein	acetone cyanohydrin	boron tribromide
allyl alcohol	acrylonitrile	boron trichloride
arsine	allyl amine	boron trifluoride
carbon monoxide	allyl chlorocarbonate	chlorine
crotonaldehyde	ammonia	chlorosulfonic acid
diketene	carbon disulfide	fluorine
ethylene oxide	carbonyl sulfide	hydrogen bromide
formaldehyde	chloroacetone	hydrogen chloride
iron pentacarbonyl	chloroacetonitrile	hydrogen fluoride
stibine	diborane	nitric acid
	dimethyl hydrazine, 1,2-	nitrogen dioxide
	dimethyl sulfate	phosphorus oxychloride
	ethylene dibromide	phosphorus pentafluoride
	hydrogen cyanide	phosphorus trichloride
	hydrogen selenide	selenium hexafluoride
	hydrogen sulfide	silicon tetrafluoride
	methanesulfonyl chloride	sulfur trioxide
	methyl bromide	sulfuryl chloride
	methyl chloroformate	tellurium hexafluoride
	methyl chlorosilane	titanium tetrachloride
	methyl hydrazine	tungsten hexafluoride
	methyl isocyanate	
	methyl mercaptan	
	n-butyl isocyanate	
	phosgene	
	phosphine	
	sulfur dioxide	
	sulfuric acid	
	tert-octyl mercaptan	
	trichloroacetyl chloride	
	trifluoroacetyl chloride	

DESTRUCTION OF BIOLOGICAL AGENTS

The CATOX operating temperature and residence time are sufficient to sterilize biological agents. Under these conditions during MUST program testing, no *Bacillus globigii (B.g.)* spores survived (Fig. 8). Similar results were recently obtained by MesoSystems Inc. in a DARPA-funded program using both *B.g.* and *bacillus thermophillus*, indicating that anthrax spores would also be destroyed. Thermal sterilization is the preferred method in the medical and food processing industries.

Typically, a high efficiency particulate air (HEPA) filters is used for biological and nuclear particulates. The efficiency is rated at 99.97% removal of particles 0.3 micrometers in diameter. After a certain time, the filter must be replaced because the pressure drop increases and to avoid biological growth that may break through the filter. With CATOX, bioprotection does not rely solely on particulate filters, and system design becomes flexible. For example, the HEPA may be retained for redundancy, or

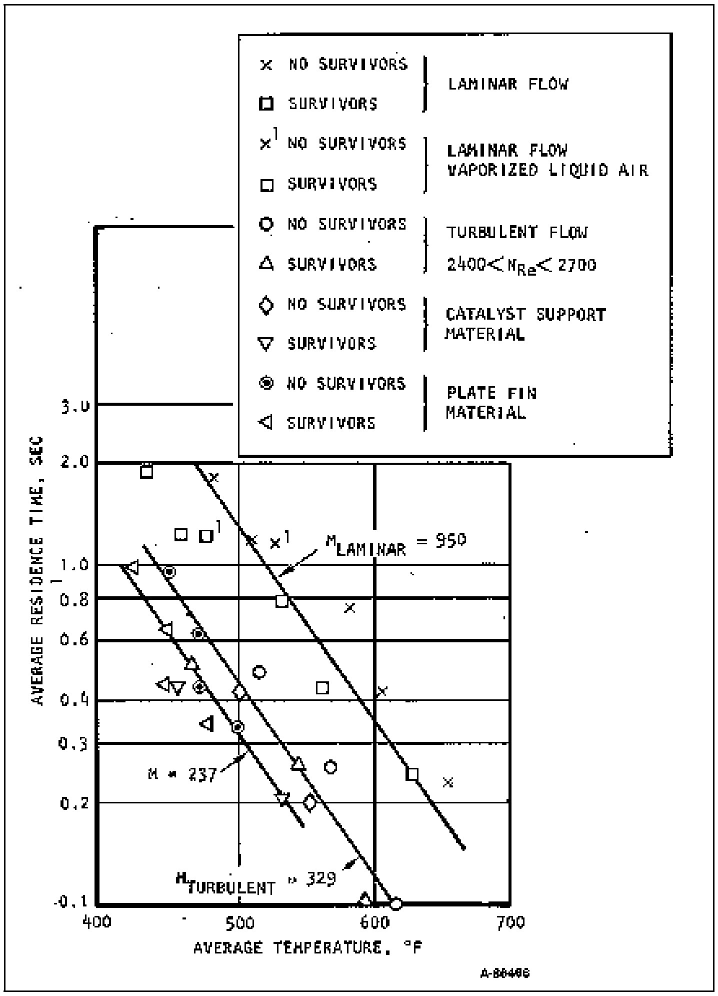

Figure 8. No *Bacillus globigii (Bg)* spore survivors under CATOX conditions.

be exchanged for a lower efficiency filter to simply catch the sterilized (and now harmless) particles. Lower efficiency filters will have lower pressure drops and thus longer maintenance intervals. If a HEPA is retained, it may be bypassed when the nuclear threat is low and used when the threat is detected. Or, if the threat scenario does not include radiological particles, the HEPA may be eliminated altogether.

COMPARATIVE ECONOMICS

There are economic and logistics benefits to the CATOX system. A preliminary cost comparison of the CATOX/PTF technology against the baseline charcoal filter is presented in Figure 9. Two scenarios were used: an extended peacetime period, and a wartime period. The operational and support costs of CATOX are much lower than the baseline filter because CATOX requires a minimum of maintenance or replacement. Therefore, CATOX costs during wartime would be 10 times less than the baseline. During peacetime, CATOX costs are estimated to be one-half that of the baseline.

Note that this model does not reflect the recent advances in CATOX/PTF technology. However, the sizing exercises in the following section help illustrate the benefits.

CATOX/PTF INTEGRATION APPROACHES WITH ECS

System Considerations

In general, CATOX/PTF size and weight decrease relative to charcoal as the air flow rate increases, which makes CATOX/PTF ideal for collective protection applications. Additional benefits occur when the CATOX/PTF is integrated with an environmental control system (ECS). Some of the system considerations are outlined in the following examples.

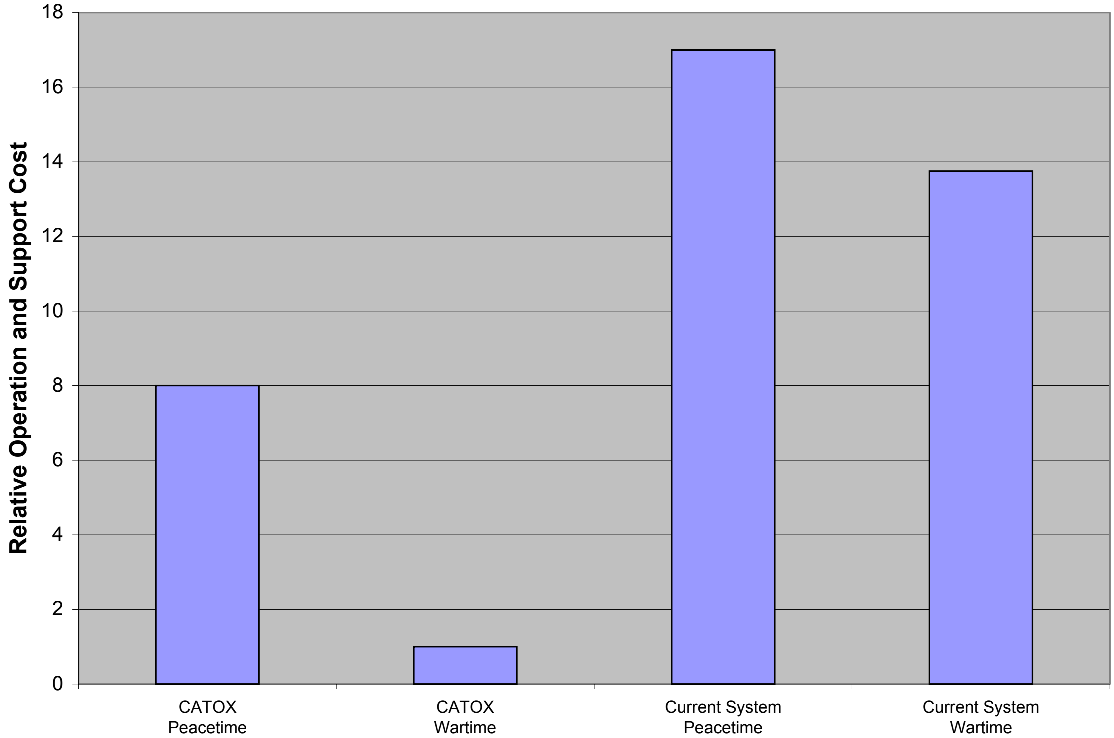

Figure 9. During a War, CATOX/PTF is an order of magnitude cheaper than the Baseline Charcoal Filter.

Armored Ground Vehicles

As the supplier of about 7,000 ECS/charcoal NBC systems for the M1A1/A2 and K77, Honeywell was in an excellent position to perform an NBC/ECS tradeoff study for the next-generation ground vehicles.

These vehicles reflect the transformed fighting force that will have the following attributes:

- ♦ Lighter and smaller, quicker deployment
- ♦ Greater survivability
- ♦ Extended operation with minimal logistics support

Because CATOX/PTF offers destruction capability for multiple attacks without maintenance, it is an ideal candidate for enhancing the survivability of the new vehicle. Many different systems were evaluated. The two most directly comparable are summarized in Table 2. Because the vehicle engine was not defined, Honeywell assumed that either a diesel or gas engine is capable of providing sufficient energy to raise the air temperature to the CATOX operating temperature.

TABLE 2. Armored Vehicle NBC System description

System	NBC Type		Avionics Cooling
	Charcoal	CATOX	
A		X	Hybrid/ LCSVCS
B	X		Hybrid/ LCSVCS

Each of the systems was sized to provide NBC protection, crew compartment overpressure, crew ventilation, heating, and cooling, and avionics cooling. The charcoal and CATOX/PTF NBC systems were sized for a generic threat scenario, where each attack included the following combination:

- low volatility agent: 2000 mg/m^3 for 10 min
- high volatility agent: 50,000 mg/m^3 for 0.5 min, 2000 mg/m^3 for 9.5 min

The estimated system weights are in Table 3. For System A, the NBC system features a CATOX/PTF sized for multiple attacks without maintenance, an exhaust gas heater, make-up air fan, precooler and fan, and recuperator, (Fig 10). The NBC system for System B features a charcoal filter sized for one attack and a make-up air fan, (Fig 11). However, to provide the same level of protection as System A, the filters in System B must be changed not only after each challenge, but also after every *suspected* challenge. Therefore, to provide the same level of protection, System B with charcoal weighs *more than 900 lbs.*, about 3 times heavier than System A with CATOX/PTF (Fig. 12). Additionally, the associated maintenance, logistics, and disposal costs of System B need to be quantified. For greater numbers of attacks, the weight difference between Systems A and B would continue to increase. Most of the NBC weight in System A is fixed, but most of the weight in System B is the charcoal filter that requires replacement.

TABLE 3. Estimated System Weight

	System A	System B
NBC System	252	89*
Crew Cooling HX	19	18
VCS/LCS	90	90
System Controller	53	53
Total	414	250
* - Weight includes only one charcoal canister. Many canisters are required to provide the same level of protection as CATOX/PTF approach. See Figure 12 for the comparison.		

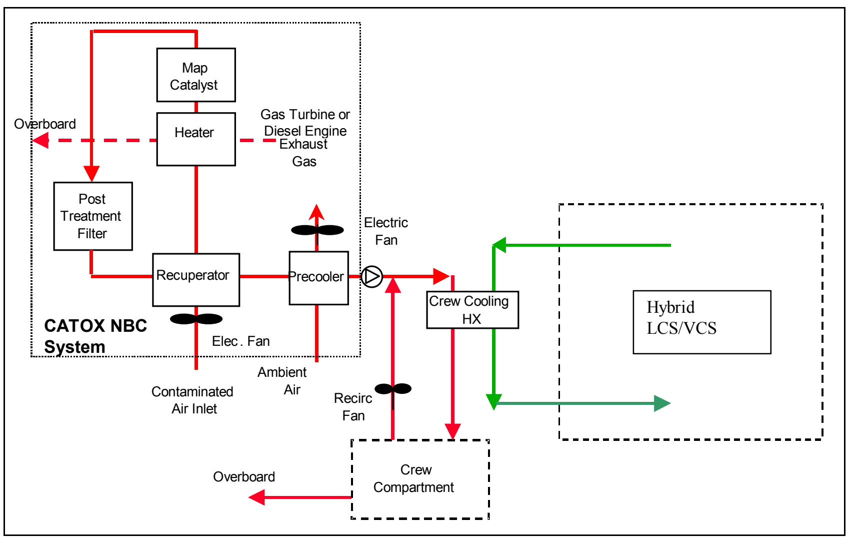

Figure 10. System A: CATOX NBC APPROACH.

Because this study supported a new vehicle, System A was designed using the engine exhaust gas to heat the make-up air to the CATOX/PTF operating temperature. The energy draw of the system is minimized, while at the same time decreasing the thermal signature of the vehicle. An electric heater can supply this energy when retrofitting a CATOX/PTF system into an existing ground vehicle.

Cargo Aircraft

Honeywell has also supported an NBC tradeoff study for an existing four engine, military transport aircraft. The goals of this study was to provide purified air to the flight deck, crew areas, and avionics/cargo compartments while minimizing the impact to an existing ECS and other systems wherever possible. The threat scenario was based on a previous study[xiii]. Both CATOX/PTF and charcoal based systems were sized.

Two CATOX/PTF NBC systems are required to protect the entire aircraft. Estimated weight for the CATOX/PTF system for multiple attacks is presented in Table 4. In contrast, the estimated weight of the charcoal based NBC system for one attack is 650 lbs. For the same number of attacks or suspected attacks, the total system weight will be 7800 lbs. because the charcoal filter requires replacement. The CATOX/PTF provides the same protection with 10 times less weight (Fig. 13). Additionally, the added charcoal filter maintenance, logistics, and disposal costs must be quantified.

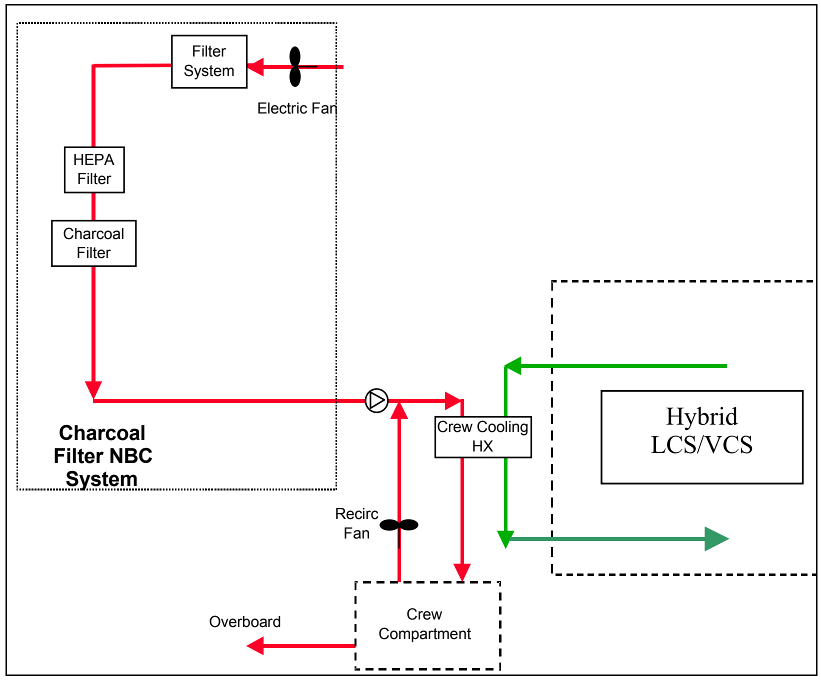

Figure 11. System B: CHARCOAL NBC APPROACH.

TABLE 4.
Estimated Weight of CATOX/PTF NBC System for Cargo Aircraft

Item	Weight (lbs)
CATOX/PTF	116
Electric Heater	14
Recuperator	200
Total per ECS	330
Total per Aircraft	660

The preferred location for the CATOX/PTF system was upstream of the ECS to take advantage of the available space and air temperature (Figure 14). Therefore, the cost of energy associated with the CATOX/PTF is a small electric heater and the weight of a recuperator, which is more than offset by the benefits of reduced logistics and maintenance. The preferred location for the charcoal system was downstream of the ECS to take advantage of the cooler air temperatures from the ECS (Figure 15).

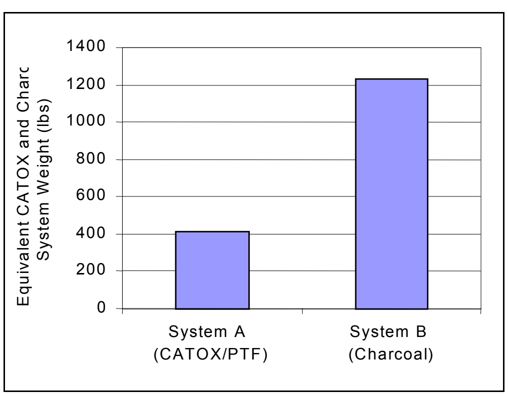

Figure 12. To provide equivalent levels of protection, System A is 3 times lighter than System B.

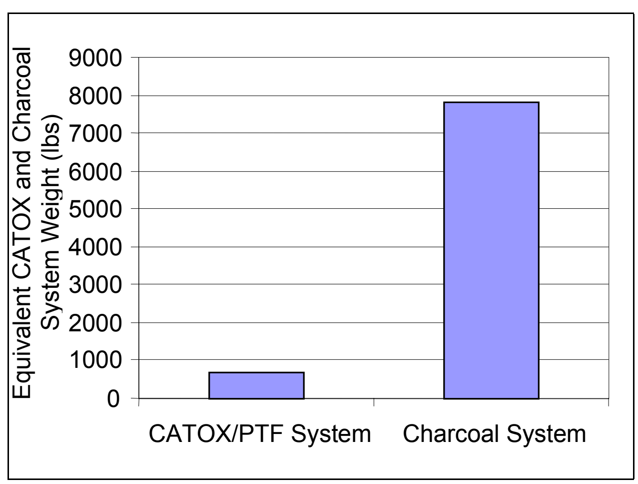

Figure 13. For multiple attacks, CATOX/PTF system weight is 10 times lighter than charcoal system.

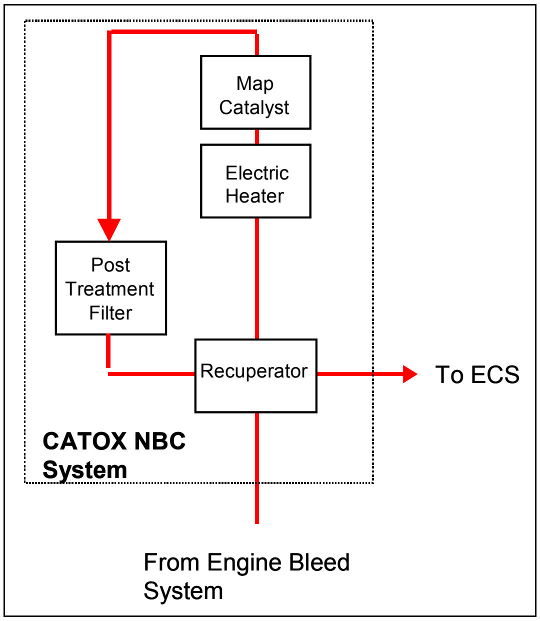

Figure 14. Cargo Aircraft CATOX/PTF/NBC System.

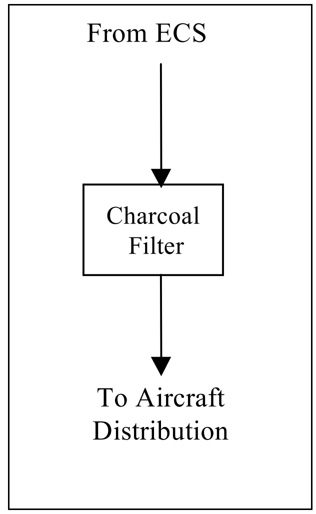

Figure 15. Cargo Aircraft Charcoal NBC System.

TRANSPORTABLE SHELTERS

The proposed Joint Transportable Collective Protection Shelter (JTCOPS) combines power generation, environmental control and NBC filtration with a clean, sheltered area. A similar design was fashioned for the MUST Hospital (Figure 16). Waste heat from the power generation unit can be used,

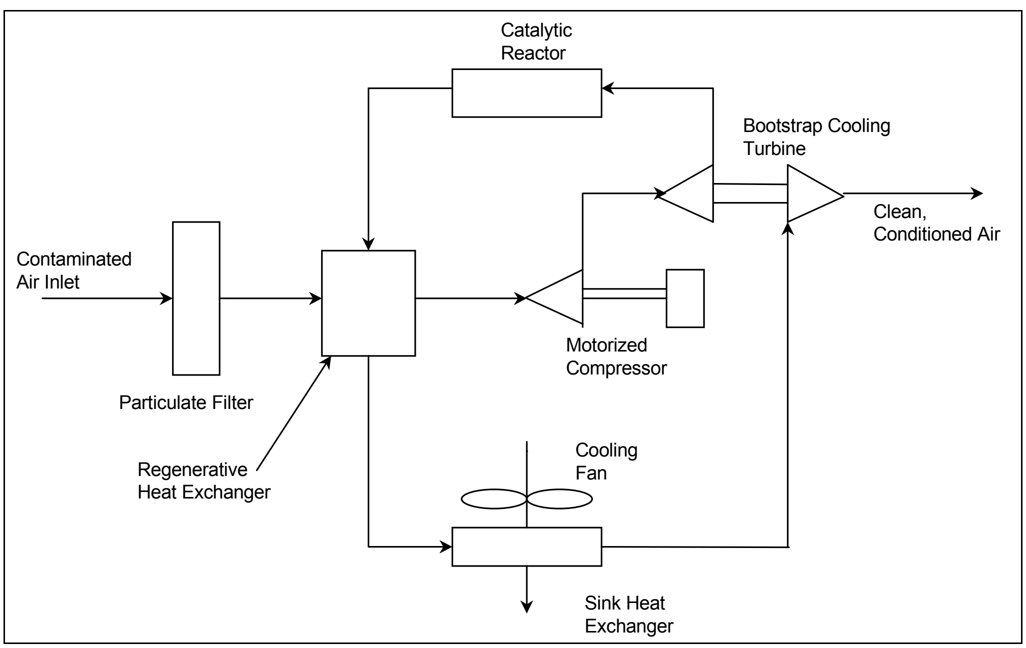

Figure 16. 400 CFM, Catalyst Based Collective Protection System Schematic.

similar to the case of the armored vehicle using engine exhaust. The weight advantage of CATOX/PTF over charcoal for multiple attacks also makes the overall system lightweight. The threat scenario for shelters can be considered as one order of magnitude less concentration than the armored vehicle scenario, as shelters would not experience a direct hit.

CONCLUSIONS

CATOX/PTF destroys greater than 99.9999% of chemical and biological agents with carbon dioxide and water as the only products. Because agents are destroyed rather than collected, no maintenance is required for multiple attacks. Thus, the life cycle costs are lower, especially during wartime. CATOX/PTF has greater potential for TIC/TIM protection than the current filtration systems. CATOX/PTF is ideally suited for collective protection because it purifies high flow rates and integrates easily with an ECS. The CATOX reactor has been matured through 30 years of testing and now has approved and specified for demilitarization of chemical agents. The PTF is a low risk item ready for full-scale validation. Potential platform applications of the CATOX/PTF include armored vehicles, cargo aircraft, and advanced shelters.

ACKNOWLEDGEMENTS

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