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DESTRUCTION TECHNIQUES FOR CFC REFRIGERANTS

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1. BACKGROUND

The release of chlorofluorocarbons (CFC) into the atmosphere has been associated with an increased level of chlorine in the earth's stratosphere. Chlorine, in turn, has been linked to a breakdown of stratospheric ozone – a component in the atmosphere that serves to filter out harmful ultraviolet (UV) radiation. As the ozone layer is thinned out, increased levels of UV radiation reach the earth's surface. Researchers and scientists believe that increased exposure to UV radiation may be harmful to human, animal and plant life.

Arising from the 1987 Montreal Protocol and the U.S. 1990 Clean Air Act, production of CFC refrigerants ceased in December 31, 1995. This international agreement to eliminate CFC production is only a first step in protecting stratospheric ozone levels. To continue safeguarding stratospheric ozone levels, existing CFC stocks must not be released to the environment; rather, they must be carefully recovered, reclaimed and reused. It has been predicted that reclaimed CFCs will be needed to operate existing refrigerators and other associated equipment over the next few years and that severe shortage are likely to occur during the interim [Telingator, 1996]. To minimize market dislocations, existing stocks of CFCs must be carefully managed.

Today, existing stocks of CFCs are valued to keep pre-1996 air-conditioning and refrigeration equipment operational. However, as a result of contamination, refrigerants may need to be destroyed. For contaminated CFCs today and in the future, an economic methodology for ultimately destroying CFCs is required. The Montreal Protocol specifies that once refrigerants are no longer required for existing uses, they must be eliminated with a destruction technology that achieves 99.99% efficiency rate. In 1992, the United Nations Environment Programme (UNEP) ad-hoc Technical Advisory Committee (TAC) on destruction technologies for ozone depleting substances recommended several thermal oxidation processes for CFC destruction. Most investigations in CFC destruction concentrate in three basic areas: thermal oxidation, chemical decomposition and "natural degradation" (e.g., biological, ultraviolet, etc.).

2. THERMAL OXIDATION DESTRUCTION

Thermal oxidation processes are employed at temperatures in excess of 900 °C. Since CFC refrigerants have low heating values and are nonflammable, supplemental fuels (generally natural gas, propane or fuel oil) are used to maintain the high-temperature oxidation process. The primary products of combustion are carbon dioxide (CO_2), water (H_2O), and halogen acids (e.g., hydrogen chloride, HCl, and hydrogen fluoride, HF) or free halogens. Products of incomplete combustion (PIC) include carbon, carbon monoxide (CO), hydrocarbons, organic acids and other toxic by-products.

Since the halogen acids are corrosive, appropriate construction materials are required to ensure that durability of the entire incineration system. Incinerators are generally lined with a refractory material to enhance the thermal destruction (minimizes radiant heat losses) and to protect the steel cylinder walls. This lining is selected to optimize the associated tradeoffs between capital and operating costs. To reduce PIC formation, adequate residence time (generally one to two seconds), high temperatures, excess oxygen and good mixing are required [UNEP, 1994].

It is recognized that thermal destruction facilities are available that can ensure 99.9999% destruction efficiency. However, in observation that 99.99% destruction efficiencies are much more widely available, the UNEP TAC recommends a 99.99% destruction efficiency as the minimum design criteria. Following is a list of several UNEP-approved thermal destruction technologies: liquid injection incinerators, rotary kiln incinerators, gaseous/fume oxidation, reactor cracking, cement kiln incinerators, and municipal solid waste incinerators.

Alternative Thermal Destruction Techniques

Other thermal oxidation methods are being investigated for destroying CFCs. One field of investigation is the very high temperature regime of plasma destruction. Small pilot facilities have been built with various types of plasma technologies. These processes use extremely high temperature plasmas (about 10,000 °C) to create reactive species for destroying chemically-stable CFCs.

Electric Arc Plasmas: The most common type of plasma technology is the electric plasma column, generated by the passage of an electric current through a gaseous medium between a cathode and an anode. This high voltage discharge creates energized electrons from an ionized corona field; the energized electrons are capable of dissociating many types of wastes. Widespread usage of electric-arc plasma technologies have been limited by several fundamental characteristics of the technology, these being: limited scale-up capability; low thermal efficiency (in terms of energy transferred to the material being processed); and limitation in electrode design; and generally-accepted design practices do not yet exist [1995 UNEP workshop].

Inductively-Coupled Radio-Frequency Plasma: Japanese have performed considerable investigations in radio-frequency plasma destruction systems and have evaluated pilot facilities since 1990 [Mizuno 1994, Suzuki 1995]. Unlike typical DC plasma generation, radio-frequency thermal plasma generation inductively heats gases in a magnetic field. The system is composed of CFC and steam feeders, a plasma generator connected to a plasma torch, a destruction reactor, a cooling chamber, a gas scrubber, a wastewater treatment unit and other pollution control equipment [Mizuno, 1994]. The CFCs decompose as they come in contact with steam, which promotes the chemical reactions.

Table 1: Comparison Data on Selective Thermal Destruction Technologies

Destruction Technology	Destruction Efficiency	Controlling Costs	Technology Commercially Available?	Advantages / Disadvantages
Liquid Injection	> 99.99%	O&M	yes	**Advantages:** - High level of acceptance and experience.
Gaseous/ Fume	> 99.99%	O&M	yes	**Advantages:** - Can easily incinerate gases. **Disadvantages:** - Large commercial base does not exist. - Acid scrubbers are still required.
Reactor Cracking	> 99.99%	Capital	yes	**Advantages:** - Rapid cooling prevents formation of dioxins and furans. - Can recover near-commercial grade HCl and HF. - Carbon dioxide production is minimized. - NOx emissions can be avoided. **Disadvantages:** - Usage of corrosion-resistant materials is extremely important.
Cement Kiln	> 99.99 %	O&M	yes	**Advantages:** - Portland cement industry offers large numbers of sites. **Disadvantages:** - Long residence times at high temperatures (e.g., > 1500°C) - CFC feed rates are restricted because of the fluoride and chloride limits in the cement product. - Potential formation of furans and dioxins.
Municipal Solid Waste	> 99.99%	O&M	yes	**Advantages:** - Technology is widely available (e.g., large existing capacity base). **Disadvantages:** - Low feed rate of CFC-containing foam (e.g., less than 2% of overall waste feed). - Some municipalities are not equipped with acid gas control systems. - No opportunity to recover HCl and HF.
Plasma Destruction	> 99.999%	Capital	no	**Advantages:** - High destruction efficiencies. - Very short reaction periods (~20 msec). - Since the destructive reaction takes place in the plasma flame, no time is required to heat the reactor; hence, can power up and down very quickly. - Unlike incineration methods, neither air nor fuel is required. Since the volume of exhaust gas produced is much smaller, the waste-gas treatment unit is more compact. - HF and HCl streams can be captured for subsequent sale into the commercial market. **Disadvantages:** - Very expensive. - Pilot plants are still to be successfully scaled-up to commercial operations.

3. CHEMICAL DECOMPOSITION OF CFCs

Most chemical decomposition technologies are not developed for practical implementation yet and research and development continue. However, catalytic processes of CFC destruction may be practical and many research efforts are focused for the development of this technology. Solvated electron technology has been commercialized by Commodore Applied Technologies, Inc. for various chemical waste destruction including CFCs [Commodore, 1997].

Various Catalytic Destruction of CFCs

Destruction of CFCs by chemical reactions using catalysts has a great potential for commercial implementation and UNEP has selected this "catalytic process" as one of the emerging technologies to be investigated. Catalytic destruction of CFCs provides several advantages and they include energy efficiency with relatively low operating temperatures, variable selectivity with selection of a catalyst and relatively simple adjustment of scale of the process [UNEP, Bickle].

However, disadvantages of the catalytic destruction processes include potential production of other harmful compounds, high yield of greenhouse gases, deactivation process of catalysts, and degradation of catalysts supports with time in presence of corrosive reaction products (e.g., HF, F, HCl, and Cl_2), or significant diminish of catalyst activity and selectivity during the deactivation process [UNEP, Bickle]. Therefore, durability of catalysts against corrosive environment should be considered in selection of a catalyst.

Acid or Metal-based Catalysts: Many groups have tested a series of catalysts for their ability to destroy CFCs. Catalysts such as silica-alumina, titanic-silica, and Y-zeolites catalysts were investigated [Karmaker]. Zeolites showed considerable destruction efficiencies with >90%. However, deactivation of zeolite catalysts due to fluorine attack poses a problem [UNEP]. Some research groups do not recommend zeolite catalysts because of their potential to form SiF_4 [Brickle]. The titanic-silica catalyst containing 60 mole% Ti exhibited the best performance among the acid catalyst mentioned above with >90% conversion [Karmaker].

Alumina-based catalysts led to severe catalyst deactivation due to fluorination of the alumina. However, zirconia-based catalysts were found to have some tolerance against fluorine species [Bickle]. A sulfated CuO/TiO_2 catalyst was shown to be effective (with >90%) in decomposing CFCs in the presence of water vapor and optionally oxygen to form CO_2 and hydrogen halides [Karmaker]. Other research group demonstrated that with their patented metal-based catalyst, >99% decomposition could be obtained. Their catalyst contains a wide range of metals and metal oxides comprising metals or oxides of the metals Pt, Rh, Pd, Ru, Mn, Cu, Cr, and Fe, and oxides of Zr, Ti, Al, W, and Si [Karmaker]. Amorphous alloy catalysts also showed efficient destruction of CFCs by hydrolysis. A research study indicated that ternary Ni-Zr-Cr alloy catalysts showed enhanced durability and catalytic activity comparing to binary Ni-Zr catalyst. The increased content of chromium enhanced the activity and elongated the life time of catalyst [Ebidzuka].

Solvated Electron Chemistry

Based on slovated electron reduction chemistry, commercial application of CFC destruction has been developed by Commodore Applied Technologies, Inc. CFCs may be destroyed by bubbling them through a solution of dissolved sodium metal in ammonia. The process involves dissolving sodium metal in anhydrous liquid ammonia to produce slovated electrons, strong reducing agents. The final products include sodium fluoride, sodium chloride and sodium formate, which are formed when the ammonia salts are treated with aqueous sodium hydroxide. The ammonia can be reused and the overall cost of the process is estimated to be low (about $3/lb of CFC). The reported destruction efficiencies is 99.99%. The main advantages of this process are the low temperatures (room temperature condition), low cost and relatively harmless by-products. One of the disadvantages is that this process is not optimum for a portable system [Satayapal, 1996].

Reductive Decomposition

Some researchers suggest that the reductive transformation of CFCs into halide ions are more reliable and safe than the oxidative incineration process.

Destruction of CFCs by Reductive Dehalogenation Using Sodium Naphthalenide: Sodium naphthalenide, which was once proved to be the most efficient for the reductive removal of chlorine atoms from organochlorine compounds, is also shown to be efficient in the complete defluorination of CFCs [Oku, 1989]. Defluorination of Freon R-113 with sodium naphthalenide in solution was studied and the reaction scheme could be described as follows: chlorines are removed in the earlier stage of the reduction, and thereafter the elimination of fluorines follows, being facilitated by the formulation of unsaturated carbon bonds [Oku, 1989].

Despite some economical disadvantages such as the stoichiometric consumption of sodium metal compared with direct incineration, advantages of this method are 1) safety, 2) easy applicability to rapid and on-site small-scale destruction where the treatment cost is not a serious problem for users and 3) no involvement of hazardous HF or F_2 in the destruction process. Furthermore, the destruction cost can also be reduced by the recycle of the reductant solution removing separated salts and naphthalene from the reactor [Oku, 1989].

Transformation of CFCs into Useful Products

It is desirable to decompose CFCs into useful products to recover marketable commodities and many studies are being conducted to find practical applications.

Mineralization and Aromatization of CFCs into Various Salts Using Sodium Oxalate: A chemical reaction which mineralize CFCs and enables the complete destruction of CFCs is investigated [Burdeniuc]. The method involves passing CFC through a packed bed of powdered sodium oxalate $(COONa)_2$, at 270 to 290 °C. The reaction products are sodium fluoride, sodium chloride, elemental carbon, and carbon dioxide [Dagani].

CF2Cl (g) + 2Na2C2O4 (g) —> C (s) + 2 NaCl (s) + 2 NaF (s) + 4 CO2 (g) [Satayapal, 1996]

Advantages of this process include use of a very simple hot-tube chemistry and inexpensive, noncorrosive reagent (Sodium oxalate is commercially available for less than $50 per kg). The process also does not tend to give uncontrollable exotherms [Burdeniuc]. The solid products can be easily handled, and sodium fluoride, which is used as a commercial fluorinating agent, can be recycled. A possible disadvantage is that the reaction also produces CO_2, which contributes to global warming through greenhouse effects. However, research efforts are finding a better reaction for destroying CFCs that does not release CO_2 [Dagani].

Production of High-purity Calcium-halides by Transformation of CFC Gases: This technology developed by Transformation Technologies, Ltd. is pending patent. The objective of this technology is to develop a "closed-loop" process to prevent atmospheric release of any waste gases or to avoid disposal of any waste products. Besides the improvement of the environmental impact, transformation of contaminated CFCs into high-purity halide salts would be economical [Johansing].

Hydrogen and oxygen gas, high-purity calcium chloride generated during the process, and a wide variety of CFC gases are injected and thermally oxidized in a tube reactor. The reaction between high-purity calcium chloride and produced hydrogen fluoride results in precipitated, high-purity calcium fluoride. Precipitated calcium fluoride is removed from the reactor by cooling fluid that is filtered [Johansing].

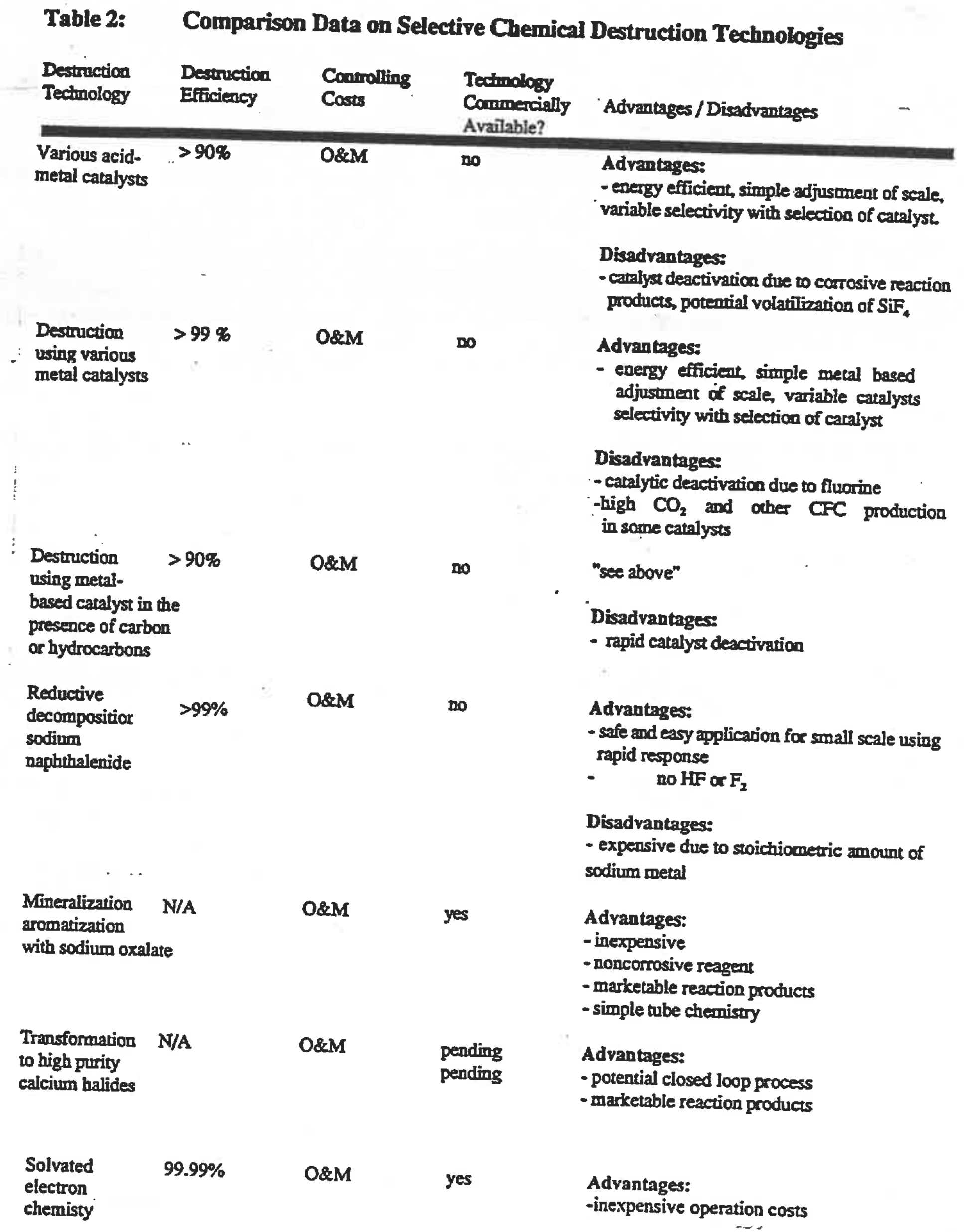


Table 2: Comparison Data on Selective Chemical Destruction Technologies

Destruction Technology	Destruction Efficiency	Controlling Costs	Technology Commercially Available?	Advantages / Disadvantages
Various acid-metal catalysts	> 90%	O&M	no	**Advantages:** - energy efficient, simple adjustment of scale, variable selectivity with selection of catalyst. **Disadvantages:** - catalyst deactivation due to corrosive reaction products, potential volatilization of SiF_4
Destruction using various metal catalysts	> 99 %	O&M	no	**Advantages:** - energy efficient, simple metal based adjustment of scale, variable catalysts selectivity with selection of catalyst **Disadvantages:** - catalytic deactivation due to fluorine -high CO_2 and other CFC production in some catalysts
Destruction using metal-based catalyst in the presence of carbon or hydrocarbons	> 90%	O&M	no	"see above" **Disadvantages:** - rapid catalyst deactivation
Reductive decompositior sodium naphthalenide	>99%	O&M	no	**Advantages:** - safe and easy application for small scale using rapid response - no HF or F_2 **Disadvantages:** - expensive due to stoichiometric amount of sodium metal
Mineralization aromatization with sodium oxalate	N/A	O&M	yes	**Advantages:** - inexpensive - noncorrosive reagent - marketable reaction products - simple tube chemistry
Transformation to high purity calcium halides	N/A	O&M	pending pending	**Advantages:** - potential closed loop process - marketable reaction products
Solvated electron chemisty	99.99%	O&M	yes	**Advantages:** -inexpensive operation costs

4. NATURAL DESTRUCTION

The destruction of CFCs by natural processes are considered innovative technologies. Natural degradation methods examined include photochemical processes (UV irradiation), biological processes (anaerobic) and sonochemical processes.

Photochemical Process

Process Technologies, Inc. (PTI) has developed a process similar to natural CFC destruction in the stratosphere. This process has not only been proven to degrade CFCs but also volatile organic compounds, hydrofluorocarbons, chlorocarbons, chlorinated solvents, aromatics, alcohols and ketones [Weigold, 1993]. The photochemical process uses low pressure ultraviolet (UV) lamps to produce a high energy wavelength similar to that of the stratosphere [Weigold, 1993]. Photons emitted from these lamps break apart the CFC molecules. The inner surface of the reactor is lined with a dry, porous cementitious liner. These liners chemically react with the gaseous free radicals produced by the photolytic destruction of the CFC molecules [Weigold, 1993]. The chemical reaction forms stable, solid reaction products that attach to the wall of the cementitious liner. The solid reaction products are not susceptible to further breakdown by UV light. The only other by-products from the photochemical destruction of CFCs are carbon dioxide, water vapors and air. One of the advantages of this process is that the destruction of CFCs takes place at a relatively low temperatures (<100 °C) and at or near ambient pressure.

Biological Process

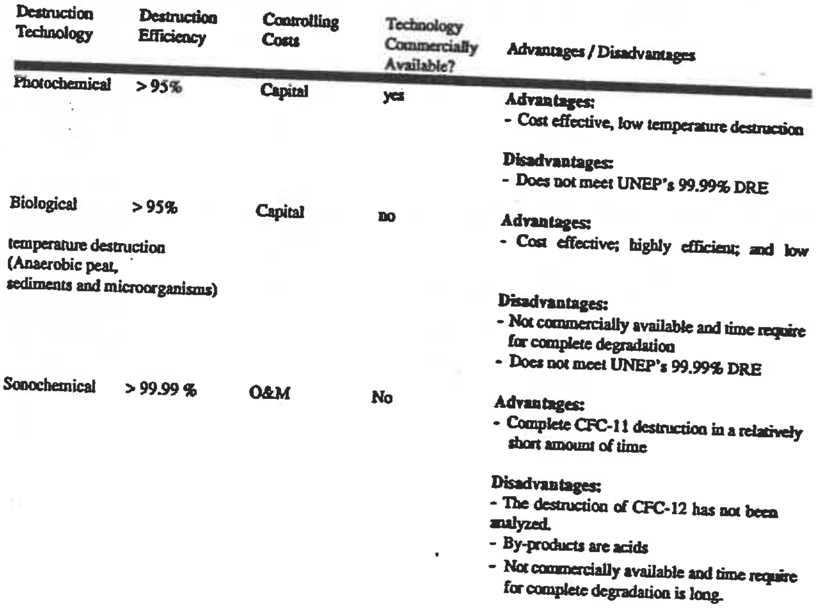
CFCs are highly volatile and disperse readily towards the stratosphere, therefore, microorganisms lack the contact time in most natural environment to readily degrade CFCs. Some small-scale test-tube/reactor experiments have been conducted to show some significant effects in the degradation of CFCs, but no large-scale projects have been addressed. Advantages of biological process is the cost effectiveness and potential in situ implementation being environmentally favorable. However, major disadvantage is the slow process to achieve the desired level of destruction.

Degradation of CFCs from Peat: CFC-11 and CFC-12 have been evaluated to ascertain their potential consumption by peat soil from a conifer swamp and a temperate bog in New York State [Bauer, et. al.]. The analysis consisted of collecting several peat cores and injecting different concentrations of CFC gases into the cores within a closed/controlled anaerobic bioreactor. This analysis show that CFC degradation occurred quicker under anaerobic methanogenic conditions and that 95% of the CFC-11 and CFC-12 can be degraded within 100 days. Gases produced as a result of the degradation of CFCs were carbon dioxide and methane.

Sonochemical Process

The sonochemical effect is due to the formation of cavitation bubbles, in fluid, which grow through several cycles of the ultrasonic wave and collapse. The collapse is adiabatic and leads to surprisingly high local pressures and temperatures. In water, the local pressure may exceed 500 atm, and the local temperature may exceed 5,000 °C [Cheng, 1992]. The localized hot spot is very short lived, which leads to extremely high heating and cooling rates, in the neighborhood of 10^9 K/s in water [Suslick, 1990]. The reactions which take place in this environment, specifically near the bubble/liquid interface, are similar to combustion, though reduction as well as oxidation has been observed. Some of the advantages are the achievement of complete destruction of CFC-11 in a short amount of time and less capital intensive than that of incineration. However, one of the disadvantages is the requirement of high operation and maintenance costs associated with creating high frequency sound.

Table 3: Comparison Data on Selective Natural Destruction Technologies



Destruction Technology	Destruction Efficiency	Controlling Costs	Technology Commercially Available?	Advantages / Disadvantages
Photochemical	> 95%	Capital	yes	**Advantages:** - Cost effective, low temperature destruction **Disadvantages:** - Does not meet UNEP's 99.99% DRE
Biological temperature destruction (Anaerobic peat, sediments and microorganisms)	> 95%	Capital	no	**Advantages:** - Cost effective; highly efficient; and low **Disadvantages:** - Not commercially available and time require for complete degradation - Does not meet UNEP's 99.99% DRE
Sonochemical	> 99.99 %	O&M	No	**Advantages:** - Complete CFC-11 destruction in a relatively short amount of time **Disadvantages:** - The destruction of CFC-12 has not been analyzed. - By-products are acids - Not commercially available and time require for complete degradation is long.

5. CONCLUSIONS

It is recognized that incineration is a demonstrated, commercially viable technology for CFC destruction; there is considerable design experience and operating guidelines available covering all engineering aspects of these systems. Hence, very few limitations need to be overcome to advance thermal technologies. However, air pollution problems associated with the stack emissions require further attention and create resistance from general public. Therefore, additional destruction technologies may need to be developed. The solvated electron technology, one of the chemical deconstruction technologies, has been commercialized by Commodore Technologies, Inc.

For new technologies, limitations to be overcome or future research needed include: development of pilot- or full-scale demonstration for commercial implementation; and improvement of destruction efficiency rates. In addition, development of catalysts and their supports with enhanced life time and durability for chemical decompostion is needed.. Futuristic trends for the destruction of CFCs will be driven by economics and meeting the 99.99% destruction efficiency rate. Technology and investment decisions should be guided by considerations such as the potential to achieve acceptable destruction efficiencies, cost-effectiveness and throughput. Catalytic, bioremediation and sonochemical destruction are viewed as futuristic viable alternatives. Perhaps the most economical alternative will be a combination of chemical, bioremediation and sonochemical processes, but until further research is proven, incineration is the choice for now.

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