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# Assessment of Incineration As A Treatment Method for Liquid Organic Hazardous Wastes

## Background Report II: Assessment of Emerging Alternative Technologies

# ASSESSMENT OF ALTERNATIVE TECHNOLOGIES

March 1985

A background report for the study by EPA's Office of Policy, Planning and Evaluation: "Assessment of Incineration As A Treatment Method for Liquid Organic Hazardous Waste."

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# EXECUTIVE SUMMARY

Assessment of incineration as a treatment method for liquid combustible and other liquid organic waste streams must take into account the availability of technologies that offer suitable treatment and destruction alternatives to conventional incinerators. This report reviews existing and emerging thermal, chemical, and biological hazardous waste destruction processes that can be used to treat or destroy the same types of liquid organic wastes that are presently destroyed in incinerators.

The processes reviewed are those that currently exist, or may exist in the next five years. Existing alternative technologies are defined as those processes other than conventional incineration that are in existence today, are suitable for treating or destroying liquid organic waste streams, and are available for commercial use. Emerging alternative technologies are innovative processes that are suitable for treating or destroying liquid organic waste streams, but have not yet been adopted for commercial use.

This report addresses the following questions:

1. What technologies other than incineration are now available, or may be available in the near future, to treat, destroy, or recycle combustible liquid hazardous wastes?
2. What is the likely commercialization rate of each of these technologies?

3. How do these technologies compare to incineration in terms of cost, capability, benefits, and environmental and human health impacts?

Each alternative technology is described in terms of the types of waste the system is capable of accepting, throughput/ capacity of the process, operational costs, anticipated environmental impact, and anticipated date for commercialization (for emerging technologies).

Although liquid organic waste streams can theoretically be treated in various thermal, chemical, and biological processes, only thermal processes were determined to be significant alternatives to conventional incineration. This is because biological and chemical processes are only in the initial stages of development, have environmental impacts that are numerous and hard to predict, are expensive, and are frequently incapable of handling combustible liquid organic hazardous wastes. Biological and chemical processes were found to be either inappropriate or suitable for only small amounts of the waste streams in question.

## EXISTING ALTERNATIVE TECHNOLOGIES

The existing thermal alternative technologies believed to be most suitable are industrial processes (cement kilns, lime kilns, and aggregate kilns), and co-combustion in industrial boilers. At the present time, susbstantially more hazardous waste is burned in industrial boilers than in incinerators.

## EMERGING ALTERNATIVE TECHNOLOGIES

Twenty-five emerging technologies were initially considered for inclusion in the report using the following criteria:

1. Is the process designed for a liquid organic waste stream?
2. Is the process at a development stage to be commercially available within five years?
3. Is the process innovative, or is the process just a modification of conventional incineration technology?

Only a few of the processes reviewed meet all three criteria and thus were determined to be relevant to this study. Those emerging processes selected for further consideration in the study are:

1. High Temperature Electric Reactor
2. Wet Air Oxidation
3. Plasma Arc
4. Supercritical Water
5. Molten Salt Reactor
6. Molten Glass Incineration

It should be noted that not all of these alternatives are able to destroy the full range of wastes handled by conventional incinerators. However, for the purpose of this study, candidate waste streams for treatment by emerging alternative technologies were identified, based on EPA data that they represent the highest volumes of waste incinerated in the United States in 1981.

## COMPARISON OF ALTERNATIVE TECHNOLOGIES WITH CONVENTIONAL INCINERATION

### Cost

Cost figures for all of the technologies, especially some of the emerging technologies, are not available. Although it varies by waste, there is a considerable reclamation of energy value in the existing alternative processes (cement kilns and boilers). Therefore, their overall costs are less than those for incineration. Another major advantage is that the use of existing facilities requires little capital investment. Among emerging processes, costs for supercritical water, plasma arc, and molten glass will exceed conventional incineration, while costs for wet oxidation, the high temperature electric reactor, and molten salt appear comparable to conventional incineration.

It should be pointed out that each of these systems offers advantages over conventional incineration for specific waste streams that may more than offset the increased costs. Some advantages are: the ability to handle small or large quantities of highly toxic wastes; smaller units to make on-site treatment economically feasible and eliminate safety factors of handling and transportation; portable units; and less production of air emissions. Thus, decisions about the probability of these technologies replacing incinerators cannot be made on the basis of cost alone.

## Throughput/Capacity

Capabilities and capacities of the various processes evaluated vary widely. Existing alternative technologies are capable of consuming significant amounts of liquid wastes, especially under existing regulations which exempt these processes from RCRA incineration standards. However, the Agency is now developing standards for these processes similar to those for hazardous waste incinerators. As a result, the capability of these processes to dispose of waste may be lessened considerably. (The potential impact of these standards on the market for incineration is not addressed in this report.)

## Commercial Status

Emerging alternative technologies will have minimal impact on the quantity of liquid hazardous waste currently destroyed in conventional processes. Although all of the emerging processes evaluated offer some technical advantages, their commercial adoption will not significantly affect the market for conventional incineration, since it is expected that these new processes will only be used on the most toxic wastes, representing only 2-3% of liquid combustible waste streams.

## Environmental Impact

More testing will be needed to determine the environmental effects of both existing and emerging alternative technologies. Environmental effects of the existing alternative technologies are currently being assessed. RCRA regulations are now being proposed for industrial boilers to assure that their operating performance is protective of human health and the environment. For most emerging alternative technologies, the environmental impacts have not been tested. In many cases, their effects are expected to be roughly comparable to those of conventional incineration.

## INTRODUCTION

The purpose of this task is to assemble available information on technologies, both existing and new, that offer alternatives to either land based or ocean incineration of liquid hazardous wastes.

The processes of interest in this task are those that currently exist, or that may exist in the next five years. They are not incineration processes, but can be used to treat or destroy the same types of liquid organic waste streams that are presently destroyed in incinerators. Existing alternative technologies are defined as those processes other than conventional incineration that are in existence today, are suitable for treating or destroying liquid hazardous waste streams, and are available for commercial use. For example, the process of burning hazardous waste as a fuel in cement kilns is an existing alternative technology because it is an alternative to conventional incineration that is practiced commercially.

Emerging alternative technologies are innovative processes that are suitable for treating or destroying liquid hazardous waste streams, but have not yet been adopted for commercial use. The process of using high temperature plasma to destroy wastes is an emerging technology, because it is still under development and has yet to be widely used for the treatment of hazardous wastes.

Another point to emphasize is that this report addresses only those processes that are intended to treat or destroy liquid organic waste streams. Many emerging technologies for hazardous waste treatment are designed to treat other types of waste streams, i.e. solids, or inorganic waste streams. Finally, for the purpose of this report, improved incineration processes such as fluidized bed incinerators or mobile incinerators are treated as conventional incineration rather than alternative technologies, and are not discussed.

The task is directed towards answering the following three questions:

1) What technologies besides incineration are available (or may be in the near future) to treat, destroy or recycle combustible liquid hazardous wastes?
2) What is the likely commercialization rate of each of these technologies?
3) How do these technologies compare to incineration in terms of cost, capability, benefits, and environmental and human health impacts?

In the subsections that follow are brief discussions of the alternative processes included in the study. Each discussion is structured as follows:

1. Brief discussion of technology involved.
2. What type of wastes is the system capable of accepting.
3. Throughput/capacity of process.
4. Operational costs.
5. Anticipated date of commercialization (for emerging technologies).
6. Environmental considerations.

## EXISTING ALTERNATIVE THERMAL PROCESSES

The following existing technologies were identified as alternative technologies that are practiced commercially and should be included in this study:

° Disposal in industrial processes (cement kilns, lime kilns, aggregate kilns)

° Co-combustion in industrial boilers

## HAZARDOUS WASTE AS FUEL IN INDUSTRIAL PROCESSES

An integral part of the production of products such as cement, limestone, and aggregate is the roasting of the feed material in large rotary kilns. The purpose of this roasting is to produce a temperature high enough for the chemical reactions necessary to produce the product to occur. Because of the high process temperatures (2000 - 2600°F), and because of the long residence times for combustion, kilns are potential thermal treatment devices for destroying many organic wastes. These wastes can be used as supplemental fuels, replacing some of the primary fossil fuels such as fuel oil or coal normally used to fire the kilns.

### Suitable Wastes

The types of waste suitable for co-combustion in kilns is very dependent upon the individual process. However, generally kilns can accept waste solvents, bottoms from solvent reclamation operations, and paint residues.

### Throughput/Capacity

1,000 - 25,000 gallons/day of liquid organic wastes can be processed in a kiln depending upon the size of the kiln and the percentages of the primary fuel replaced by the waste fuel.

COST PER UNIT OF WASTE PROCESSED

Costs can vary from zero, reflecting a company's accepting a very high energy waste solely for its fuel value, to some 20 to 25 cents per gallon.

ENVIRONMENTAL DATA

Assessments conducted by EPA and others have produced mixed results on the environmental and health effects of combusting waste chemicals in cement kilns. However, they indicate that when a kiln is operated properly, its emissions are comparable to those of a well operated incinerator, and meet emissions standards for incineration.

Anticipated Date of Commercialization

Technology is currently being utilized on a commercial basis. An estimated 3.5 million tons of waste went to industrial processes in 1981 (1).

INCINERATION OF HAZARDOUS WASTES IN POWER BOILERS

Under RCRA, the regulations and specific process performance standards for hazardous waste incineration do not apply to the use of combustible hazardous waste as fuels in energy recovery operations such as power boilers. In part because of this regulatory situation and because of the obvious attractiveness of reclaiming energy from waste, significant quantities of liquid hazardous waste are disposed of in industrial boilers. EPA studies have estimated that 3.5 million tons of hazardous wastes were disposed of in this manner in 1981, more than twice the amount disposed of in incinerators that year (1).

There are currently about 400,000 boilers of all types in the U.S. including industrial, commercial, residential and off-site power. Of these boilers, about 240,000 can be classified as industrial installations. This figure includes boilers of all types and all sizes. Table 1 breaks down the industrial boiler population by fuel type and size.

Table 1

Capacity (BTU/HR) of Industrial Boilers by Fuel Type (1975)

| Fuel Type | $< 10^6$ | $10^6$ and $< 10^7$ | $> 10^7$ |
|---|---|---|---|
| Stoker Coal | 1,800 | 9,200 | 5,200 |
| Pulverized Coal | 300 | 1,800 | 1,500 |
| Residual Oil | 8,100 | 46,000 | 11,500 |
| Distillate Oil | 14,200 | 37,300 | 2,200 |
| By-Product Gas | 400 | 2,000 | 11,300 |
| Natural Gas | 15,900 | 57,700 | 11,300 |

Most of these boilers are very small natural gas or oil-fired firetube or cast iron units used for space heating. Such installations are generally package units and do not easily lend themselves to either waste firing or to the fuel blending required in waste co-firing. However, examination of Table 1 shows that there are about 43,000 industrial boilers in the U.S. with capacities larger than 10 million BTU's per hour. These larger boilers have the greatest potential for use in hazardous waste destruction processes.

It is more the rule than the exception that large organic chemicals producers operate one or more boilers on the plant premises. Some of these plants use boilers for on-site destruction of organic chemical wastes; the number of boilers used is not known.

Suitable Wastes

Boilers are generally capable of accepting any lowly halogenated liquid organic waste stream. It is possible to burn up to 3% halogenated wastes, but usually because of corrosive waste streams only approximately 1% halogens are burned.

Process Throughput

Depends on the size of the boiler. A large boiler using organic wastes to replace 25% of the feed would consume 500 gallons per day of waste. However, studies have indicated that 10% of the feed is more typical.

Cost Per Unit of Waste Processed

No specific cost figures were located. However, given that most waste that is burned in boilers is burned on-site and replaces conventional incineration, the additional cost is minimal compared to providing for a separate facility for incineration of the waste.

Anticipated Date of Commercialization

Burning waste in boilers is widely practiced. The EPA has estimated that 1300 boilers utilized hazardous waste as fuel in 1981 (1).

Environmental Data

The Agency is presently supporting a large research program to obtain environmental effects information on burning wastes in boilers. Field test data have shown that boilers can achieve waste destruction efficiencies comparable to those of incinerators. Current evaluations are underway to determine emissions from boilers operating at less than optimum conditions.

## EMERGING ALTERNATIVE TECHNOLOGIES

Currently there are many new processes in various stages of development for treating and destroying all types of hazardous waste. Some of these processes are essentially improvements on conventional treatment and destruction methods. Examples of such are fluidized bed incineration, which is considered by many to be an improvement over conventional incineration. Other processes represent entirely new approaches to waste treatment. The former group are included with conventional methods and not addressed, and the latter considered emerging technologies.

The processes discussed in this section were compiled from responses to two national solicitations for new hazardous waste treatment ideas, from several literature reviews, and from contact with experts in the field. This procedure identified many processes that represented new approaches to hazardous waste treatment and destruction. However, only a few of the processes identified were determined to be relevant to this study, i.e. designed for liquid organic wastes and sufficiently close to commercialization to significantly affect within the next five years the waste management practices of the Country as a whole. A list of the processes reviewed for this study is attached as Appendix A. Those processes determined to be emerging processes relevant to this study are:

- High Temperature Electric Reactor
- Molten Salt Reactor
- Plasma Arc

- Wet Oxidation
- Supercritical Water
- Molten Glass Incineration

It should be noted that none of these alternatives are able to destroy the full range of wastes now handled by conventional incinerators.

## Candidate Waste Streams

The following waste streams were identified as candidate streams for treatment by alternative technologies. This selection was based on EPA data indicating that these waste streams represented the highest volumes incinerated in the U.S. in 1981.

| EPA Waste # | Description |
|---|---|
| D001 | Hazardous waste that exhibits characteristic of ignitability |
| D002 | Hazardous waste that exhibits characteristic of corrosivity |
| D003 | Hazardous waste that exhibits characteristic of reactivity |
| F001-F002 | Spent halogenated solvents |
| F003-F005 | Spent non halogenated solvents |
| K049 | Slop oil emulsion solids from the petroleum refining industry |
| K051 | API separate sludge |
| | PCB's |

TABLE 3

ALTERNATE TECHNOLOGY VS WASTE STREAMS

| | D001 | D002 | D003 | F001-002 | F003-005 | K049 | K051 | PCB |
|---|---|---|---|---|---|---|---|---|
| Incineration | X | X | X | X | X | X | X | X |
| Industrial Processes | X | | | X | X | X | | X |
| Boiler Co-combustion | X | | | | X | | | |
| High Temp. Electric Reactor | X | | | X | | X | | X |
| Molten Salt | X | | | X | | X | | |
| Plasma Arc | X | | | X | | X | | X |
| Wet Oxidation | X | | | X* | | | | |
| Molten Glass | X | | | X | | X | | X |
| Supercritical $H_2O$ | X | | | X* | | | | |

* In Aqueous Solutions

## HIGH TEMPERATURE ELECTRIC REACTOR

This process utilizes a vertical reactor heated by electrodes implanted in the walls to pyrolize organic wastes. The process is offered by two companies, Thagard Research, which developed the process, and Huber Corporation, which acquired rights to the process and introduced several modifications.

The process utilizes a reactor with a core enclosed by porous refractory material. Carbon electrodes implanted in the wall of the reactor heat the reactor core to radiant temperatures. Heat transfer is accomplished by radiation coupling from the core by means of a gaseous blanket formed by flowing nitrogen through the walls of the core. In the process organic compounds are rapidly heated to temperatures in the range of 3800° - 4400°F and destroyed.

In the Huber process product gas and waste products pass through two port reactor treatment zones which provide for additional exposure to high temperatures and for product gas cool down.

### Suitable Wastes

The process is primarily designed to pyrolize organics attached to particulates such as carbon black or soil. However, the developer claims that recent tests have shown the process is also effective for liquid refractory waste streams such as carbon tetrachloride.

### Throughput/Capacity

The Huber unit will process from 75 to 125 pounds of contaminated solids per minute. Hard numbers are not available for pure liquids. However, capacity would be less.

## Costs

Costs information is not available. However, the Huber Corporation claims the cost of operating a unit is comparable to conventional incineration.

## Anticipated Date of Commercialization

Mid summer 1985.

## Environmental Data

Huber recently completed a test of the process which showed that DRE's far in excess of the 99.99% RCRA requirements can be obtained.

## MOLTEN SALT

### Process Description

Molten-salt destruction is a method of burning organic material while, at the same time scrubbing in situ any objectionable byproducts of that burning and thus preventing their emission in the effluent gas stream. This process of stimulating combustion and scrubbing is accomplished by injecting the material to be burned with air or oxygen-enriched air, under the surface of a pool of molten sodium carbonate. The melt is maintained at temperatures on the order of 900°C, causing the hydrocarbons of the organic matter to be immediately oxidized to carbon dioxide and water. The combustion byproducts, containing such elements as phosphorous, sulfur, arsenic and the halogens, react with the sodium carbonate. These byproducts are retained in the melt as inorganic salts rather than being released to the atmosphere as volatile gases. In time, inorganic products resulting from the reaction of organic halogens, phosphorous, sulfur, etc., build up and must be removed from the molten bed to retain its ability to absorb acidic gases. Ash introduced by the waste must be removed to preserve the fluidity of the melt. An ash concentration in the melt of about 20% by weight provides an ample margin of safety to maintain melt fluidity.

Suitable Wastes

The Molten Salt process is designed for solid and liquid waste streams. It is especially applicable to highly toxic wastes and to highly halogenated waste streams. Waste streams with high percentages of ash and non-combustibles are not very good for the system since such waste makes it necessary to replace the molten bed more often.

Process Throughput

A new pilot scale facility capable of processing 80 to 200 pounds of waste per hour has recently been constructed. No commercial scale units have been built to date.

Costs Per Unit Processed

No cost data available.

Anticipated Date of Commercialization

This process has been demonstrated successfully with many different liquids and slurries, and is currently available for commercial use. No commercial units are currently operational.

Environmental Impacts

A variety of chemical wastes have been successfully incinerated in bench-scale molten salt combustors. Destruction efficiencies for organic chemicals, pesticides and chemical warfare agents ranged from 99.99% to 99.999999%. Tests were performed by Rockwell International for the State of California (2).

PLASMA ARC TECHNOLOGY

One of the emerging technologies receiving much attention is plasma arc technology, which is a process using the extremely high temperatures of plasmas to destroy hazardous waste.

A plasma is a substance consisting of charged and neutral particles with an overall charge near zero. A plasma arc is generated by electricity and can reach temperatures up to 50,000°F. When applied to waste disposal, the plasma arc can be considered as an energy conversion and energy transfer device. The electrical energy is transformed into a plasma. As the activated components of the plasma decay, their energy is transferred to the waste materials exposed to the plasma. The wastes are ultimately decayed and destroyed as they interact with the decaying plasma.

In a mobile prototype of a patented process, a five hundred kilowatt plasma device is fitted to one end of a stainless steel reaction chamber and mated to a hollow graphite core to form an atomization zone. Residence time in this atomization zone is approximately five hundred micro-seconds. The reaction chamber serves as the equilibration zone where the atomized species recombine to form new simple non-hazardous products. This zone is equilibrated at a temperature range of 1200-1800 Kelvin and the residence time in this zone is approximately one second. All hardware is designed to be located within a forty five foot long moving van type trailer.

Suitable Waste Streams

Plasma arc technology is designed for highly toxic liquid waste streams. The operation of the process is not significantly impacted by the degree of halogenation of a waste stream.

Process Throughout

A unit currently being demonstrated through partial support of the Agency will process 600 lbs. of waste per hour. This unit is sized to be operated commercially.

## Cost Per Unit of Waste Processes

Cost figures not available.

## Analytical Date of Commercialization

A commercialization scale unit is to be operating within 1-3 years.

## Environmental Data

No environmental data from a commercial scale unit is currently available. A current demonstration in the State of New York is to produce information on destruction efficiency, and characterization of emissions.

# WET AIR OXIDATION

## Process Description

Wet air oxidation is a process for oxidizing organic contaminants in water. Wet air oxidation refers to the aqueous phase oxidation of dissolved or suspended organic substances at elevated temperatures and pressures. Water, which makes up the bulk of the aqueous phase, serves to modify oxidation reactions so that they proceed at relatively low temperature (350°F to 650°F) and at the same time serves to moderate the oxidation rates removing excess heat by evaporation. Water also provides an excellent heat transfer medium which enables the wet oxidation process to be thermally self-sustaining with relatively low organic feed concentrations.

An oxygen-containing gas, usually air, is bubbled through the liquid phase in a reactor used to contain the process, thus the commonly used term "wet air oxidation" (WAO). The process pressure is maintained at a level high enough to prevent excessive evaporation of the liquid phase, generally between 300 and 3000 psi.

A wastewater stream containing oxidizable contaminants is pumped to the system by means of a positive displacement-type pump. The wastewater passes through a heat exchanger which preheats the waste by indirect heat exchange with the hot oxidized effluent. The temperature of the incoming feed is increased to a level necessary to support the oxidation reaction in the reactor vessel. Air and the incoming liquid are injected into the reactor where the oxidation begins to take place. As oxidation progresses up through the reactor, the heat of combustion is liberated, increasing the temperature of the reaction mixture. This heat of oxidation is recovered by a heat exchange that utilizes the incoming feed. Thus it is thermally a self-sustaining operation. After energy removal, the oxidized effluent, comprised mainly of water, carbon dioxide, and nitrogen is reduced in pressure through a specially designed automatic control valve.

Of all variables affecting wet air oxidation, temperature has the greatest effect on reaction rates. In most cases, about 300°F is the lower limit for appreciable reaction, about 482°F is needed for reaction to the 80 percent reduction of Chemical Oxygen Demand (COD) range, and at least 572°F is needed for 95 percent reduction of COD or better reaction within practical reaction time.

The use of catalysts have been evaluated for improving the destruction efficiency of WAO. However, there are no commercial application of WAO utilizing a catalyst at the present time.

Suitable Wastes

The process is designed primarily for very dilute aqueous wastes which are too dilute to incinerate economically yet too toxic to treat biologically. WAO also has application for inorganic compounds combined with organics. It is not very effective in oxidizing highly refractory chlorinated organics.

Process Throughput

An existing unit is being demonstrated on various waste streams in California. This unit can process up to 10 gallons per minute.

Cost Per Unit of Waste Processed

A cost range of 5 cents to 10 cents/gallon of waste processed is cited by one of the developers of a wet oxidation process. These costs are for the 10 gallon per minute system. Costs for larger systems are not available.

Anticipated Date of Commercialization

Technology is available now. Wider adoption could occur within the next two years, however, application would be limited to aqueous wastes that cannot be economically incinerated. Adoption will also depend on the destruction efficiency and whether post treatment is required.

Environmental Effects

Limited environmental data from bench-scale tests is available. However, the USEPA-ORD, under a cooperative agreement with the State of California, is currently evaluating a full-scale (10 GPM) unit (3). All of the full scale tests have not been completed; wastes being tested include: cyanide wastes, phenolic wastes, sulfide wastes, non-halogenated pesticides and solvent still bottoms.

## MOLTEN GLASS INCINERATION

### Process Description

The integral part of this process is an electric furnace approximately 22' long and 3' wide that has a pool of molten glass covering the bottom. This type of furnace is used extensively in the glass manufacturing industry to produce glass. When used as a waste incinerator the extremely high temperatures in the combustion chamber destroy organic waste streams.

Waste materials, both combustible and non-combustible, are charged directly into the combustion chamber above the pool of molten glass. The waste can either be contained in fiberboard boxes, or uncontained in loose form. Electrodes immersed in the pool maintain the temperature of the pool of molten glass above 2300° (1260°C). Combustible waste are oxidized above the pool, and inorganics and ash fall onto the pool where they are melted into the glass. Combustion off gases pass through ceramic filters which are themselves charged into the molten glass when they are no longer effective.

### Suitable Wastes

Any combustible waste is acceptable. Degree of halogenation is not a consideration. However scrubbers will be required for HCl emissions.

### Process Throughput

Since this technology is used in the glass manufacturing industry, existing units are capable of processing from 100 pounds per hour to 21,000 pounds of raw materials per hour. However these have not been demonstrated as devices for destroying hazardous wastes.

Cost Per Unit of Waste Processed

No cost figures were available.

Environmental Effects

Although no actual data on hazardous waste is available, the fact that the unit uses ceramic filters for air emissions and encapsulates the inorganic residues in a glass slag seems to indicate that environmental emissions would be minimal and at least comparable to incineration. However, this remains to be tested.

SUPERCRITICAL WATER

Process Description

In the supercritical water process an aqueous waste stream is subjected to temperatures and pressures above the critical point of water, i.e. that point at which the densities of the liquid and vapor phase are identical. (For water the critical point is 379°C and 218 atmospheres). In this supercritical region water exhibits unusual properties that enhance its capability as a waste destruction medium. Because oxygen is completely miscible with supercritical water, the oxidation rate for organics is greatly enhanced. Also inorganics are practically insoluble in supercritical water. This factor allows the inorganics to be easily removed from the waste streams. The result is that organics are oxidized extremely rapidly and the resultant stream is virtually free of inorganics.

A patented process has been developed that incorporates the properities of supercritical fluids to oxidize organic contaminants in aqueous streams.

The following is a brief summary of the process.

a. Waste is slurried with make-up water to provide a mixture of 5 percent organics. The mixture is heated using previously processed supercritical water and then pressurized.

b. Air or oxygen is pressurized and mixed with the feed. Organics are oxidized in a rapid reaction. (Reaction time is less than 1 minute.) For a feed rate of 5 percent by weight of organics, the heat of combustion is sufficient to raise the oxidizer effluent to 500°C.

c. The effluent from the oxidizer is fed to a salt separator where inorganics are removed by precipitation.

d. Waste heat from the process can be reclaimed to provide sufficient energy for power generation and high pressure steam.

Suitable Waste Streams

Supercritical water processes are designed for aqueous waste streams with high levels of inorganics and toxic organics. The system's capability for treating aqueous waste streams with high percentages of halogenated material has not yet been demonstrated.

Process Throughput

A unit is currently being demonstrated to treat from 1,000 to 2,000 gallons per day of aqueous wastes.

Cost Per Unit of Waste Processed

No cost figures are available.

Anticipated Date of Commercialization

The developer of the system claims that commercial scale units will be available in 1-3 years.

## Environmental Impact

Bench scale tests on a variety of hazardous materials have indicated DRE's of 98.5 to 99.8. A demonstration unit is currently being evaluated by industry, and will generate environmental data for a larger unit.

## BIOLOGICAL TREATMENT

Biological treatment encompasses the use of living organisms or their by-products, such as enzymes, to effect destruction or detoxification of hazardous waste. Procedures ranging from acclimation to genetic engineering are used to develop appropriate organisms to accomplish the degradation process. In most cases a "reactor" of some type is constructed to provide a suitable environment for the required biochemical reactions. The reactor may be as simple as a storage lagoon or as complex as a fermentation tanks, with ability to control temperature, pH, moisture, nutrients, oxzygen, off-gases, mixing with the waste and/or separation from the treated material. Land treatment and composting are low tech applications of biological treatment. Most biological treatment systems are suitable only for treatment of very dilute aqueous wastes (organic content <1% by weight) or for detoxification of contaminated soils or sediments, especially when the detoxification can be accomplished while leaving the soil or sediment essentially in place. No significant use of biological treatment for combustible liquid hazardous wastes is anticipated in the foreseeable future.

The potential environmental impacts of biological treatment are numerous and sometimes difficult to predict. Biological processes tend to be slow, thus contaminants with even low to moderate volatility can be transferred to the atmosphere from lagoons, composting facilities, land treatment or spray irrigation. Pollutant transfer by air stripping is an important concern in any aerated biological treatment process. Even very low levels of some toxic compounds may remain in biological treatment residuals could warrant regulation. The pollutants are too dilute to be effectively used as a food source by suitable organisms in activated sludge, composting, anaerobic digestion or land treatment systems. The eventual use or disposal of the biological residuals thus becomes a hazardous waste concern. The complexities of biological processes result in frequent upset or out of control conditions and corresponding reductions in pollutant removal efficiencies. Such excursions could not be tolerated when treating hazardous wastes. Finally, estimating the environmental impacts of introducing genetically engineering organisms into the open environment is a difficult and controversial problem. It is unlikely that biological treatment based upon genetically engineered organisms will rapidly develop for commercial use.

## Chemical Treatment

Major chemical treatment processes applied to hazardous waste include chemical oxidation or reduction, hydrolysis, neutralization and photolysis. Precipitation as a separation technique may be accomplished by using one or more of these treatment processes. Common applications for hazardous waste treatment are oxidation of phenol or cyanide in aqueous wastes, neutralization of corrosive wastes such as pickling liquors or caustic wastes, and detoxification of contaminated soils. Combustible liquid hazardous wastes are generally not good candidates for chemical treatment, although dehalogenation may in special cases result in the recycling or recovery of a waste.

Cost and environmental impact are important considerations in applying chemical treatment technology.

The cost of reactants can be signficatn if large quantities of the target pollutant are to be processed. Often, large doses of reactants are necessary to destroy even low concentrations of hazardous constituents, because of interference from non-hazardous components or, as is often the case with ozonation, the difficulty of effectively mixing the reactants with the waste to achieve stoichiometric amounts of oxidant. For example, the necessity of using large doses of degalogenating chemicals on dioxin contaminated soils presents a current research problem of how the dehalogenation reaction can be enhanced to effectively use near stoichiometric amounts of reactants.

Operational and capital costs are also a factor. Energy requirements and thus costs increase as additional temperature and pressure are required. As a result, capital costs also increase because high temperature, pressure and corrosivity mandate the use of exotic construction materials.

Chemical treatment poses several problems with regard to environmental impact. The safety of reactions which produce heat or emit gases can be a significant problem. Also, the reaction by-product may be hazardous. The process may also cause disposal problems, because adding chemicals to waste often increases the amount of material ultimately requiring disposal. Eventhough these detoxified residuals are non-hazardous, their disposal would be costly and could present a public relations problem.

Therefore, in terms of cost and environmental impact, incineration of combustible hazardous waste will continue to have advantages over chemical processes currently being used or under development.

# APPENDIX A

## EMERGING PROCESSES CONSIDERED

| PROCESS | PROCESS IS DESIGNED TO: | INCLUSION/EXCLUSION CRITERIA | | |
|---|---|---|---|---|
| | | DESIGNED FOR LIQUID WASTE STREAM | AVAILABLE WITHIN 5 YEARS | INNOVATIVE TECHNOLOGY |
| *1. High Temp. Electric Reactor | pyrolize organics off surface of particles using high temp. radiant heat | X | X | X |
| *2. Molten Salt Reactor | destroy organics using a molten bed of sodium carbonate | X | X | X |
| 3. Rotary Pyrolyzer | detoxify organic sludges in a quiescent environment | | X | X |
| 4. Low Temp. Fluid Bed | utilize limestone and a catalyst with high velocity fluidizing air in fluid bed processes | X | | |
| 5. Multi Solid Fluid Bed | destroy solids and liquids in a dense bed of large particles | X | X | |
| *6. Molten Glass | destroy organics using glass manufac-turing furnace | X | X | X |
| 7. Catalytic Dehalogenation | to replace halogen atoms with hydrogen atoms in presence of a catalyst | X | | X |
| 8. High Temp. Pyrolysis with $O_2$ | destroy organics in a saturated oxygen furnace | X | | X |

* Process Selected

| PROCESS | PROCESS IS DESIGNED TO: | INCLUSION/EXCLUSION CRITERIA | | |
|---|---|---|---|---|
| | | DESIGNED FOR LIQUID WASTE STREAM | AVAILABLE WITHIN 5 YEARS | INNOVATIVE TECHNOLOGY |
| 9. Corona Glow Processing | utilize a plasma with a high volumetric flow rate of process gas | X | | X |
| 10. Fluid Phase Oxidation | destroy toxic organics in aqueous waste streams in the presence of oxygen | X | | X |
| 11. Circulating Bed Waste | utilize a hot cyclone chamber in conjunction with a traditional packed bed incinerator | X | X | |
| 12. Aqueous Phase Alkaline Destruction | convert organic solids to oil in a thermo-chemical process | X | | X |
| 13. Fluid Bed Incinerator | destroy homogenous waste in a traditional fluidized bed reactor | X | X | |
| 14. Microwave Plasma Detoxification | utilize microwaves within a plasma to oxidize toxics | X | | X |
| 15. Plasma Temp. Incinerator | burn PCB waste in a pressurized stream of preheated oxygen | X | X | X |
| 16. Mobile Incinerator | rotary kilns or liquid injection units on wheels | X | X | |
| 17. O'Connor Combustor | advanced traditional incinerator technology using a hollow water-cooled steam cylinder | | X | |
| *18. Plasma Arc | extremely high temperatures produced by plasma generators | X | X | X |

| PROCESS | PROCESS IS DESIGNED TO: | INCLUSION/EXCLUSION CRITERIA | | |
|---|---|---|---|---|
| | | DESIGNED FOR LIQUID WASTE STREAM | AVAILABLE WITHIN 5 YEARS | INNOVATIVE TECHNOLOGY |
| *19. Wet Oxidation | use high temperatures and pressures to oxidize organic contaminants in aqueous streams | X | X | X |
| *20. Supercritical Fluid Oxidation | utilize a high temp. high pressure wet oxidizer | X | X | X |
| 21. "Cyclin" Cyclone Incinerator | include a potential-like flow at pre-mixed fuel, waste, and air within a combustion chamber | X | | |
| 22. Consertherm Rotary Kiln Oxidizer | modify a conventional rotary kiln approach thermal destruction | X | X | |
| 23. Joule-Heated Glass Melter | utilize the material being heated as the resistance element in an electrical circuit | X | | X |
| 24. Fast Rotary Reactor | increase contact between solids and gases by modification of rotary kiln design | X | X | |
| 25. Burlesan/Kennedy Submerged Reactor | utilize underground wells to achieve conditions for supercritical water reactor | X | | X |

## REFERENCES


1 EPA 530/SW-84-005, April 1984; "National Survey of Hazardous Waste Generators and Treatment, Storage and Disposal Facilities Regulated under RCRA in 1981".

2 EPA/California Cooperative Agreement R808908, August 1981; "Molten Salt Destruction Process: An Evaluation for Application in California".

3 EPA/California Cooperative Agreement Project, "Demonstration of Wet Air Oxidation of Hazardous Waste", Proceedings of Tenth Annual EPA Hazardous Waste Research Symposium, April 1984.





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