

# INNOVATIVE SITE REMEDIGATION TECHNOLOGY

DESIGN & APPLICATION

Volume 6

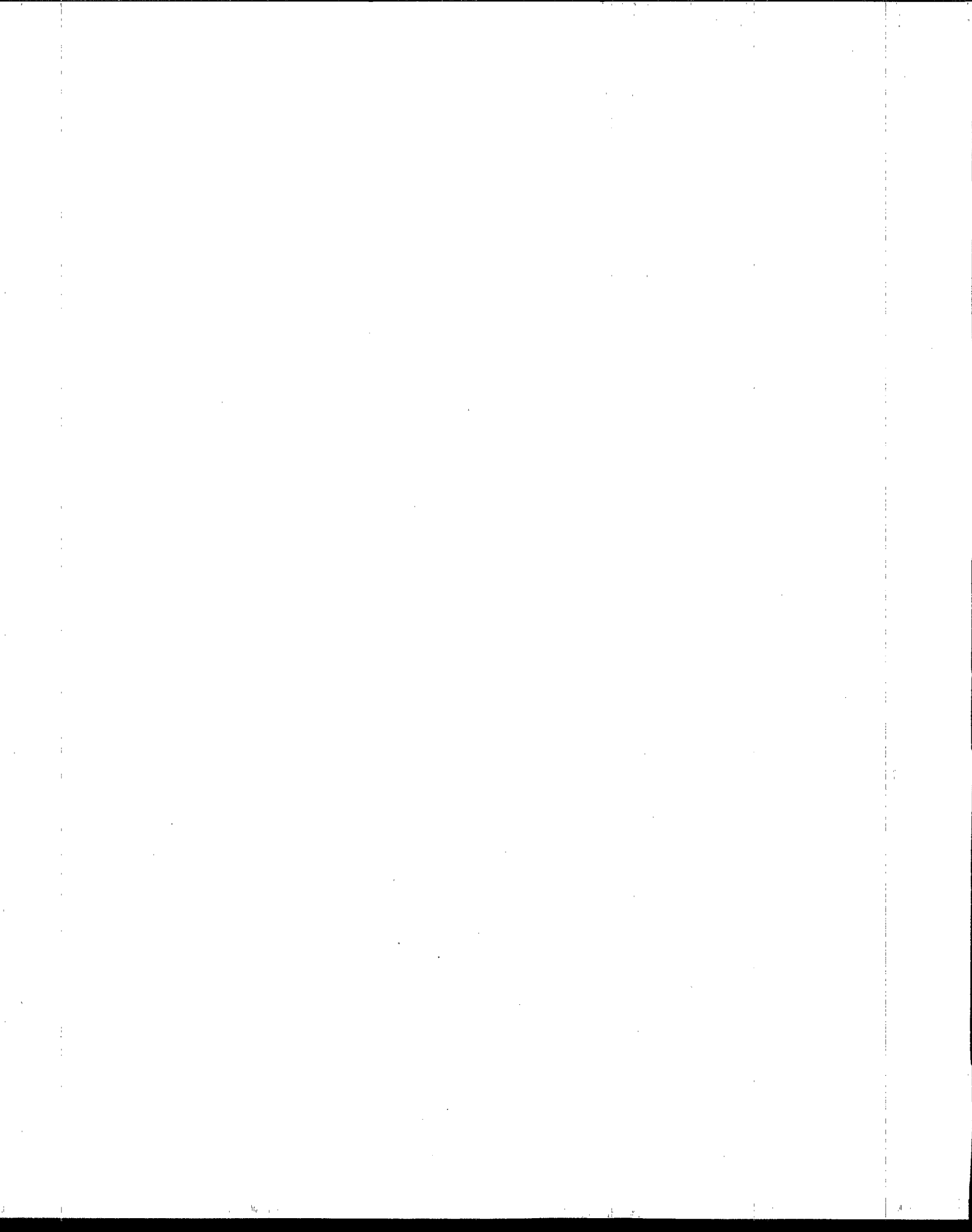
## Thermal Destruction

Prepared by the American Academy of Environmental  
Engineers under a cooperative agreement with the U.S.  
Environmental Protection Agency



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Academy of Environmental  
Engineers under a  
cooperative agreement with  
the U.S. Environmental  
Protection Agency

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INNOVATIVE SITE  
REMEDiation TECHNOLOGY:  
DESIGN AND APPLICATION  
**THERMAL DESTRUCTION**

One of a Seven-Volume Series

Prepared by WASTECH®, a multiorganization cooperative project managed by the American Academy of Environmental Engineers® with grant assistance from the U.S. Environmental Protection Agency, the U.S. Department of Defense, and the U.S. Department of Energy.

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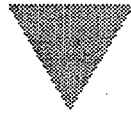
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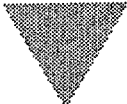
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This document was reviewed by volunteer members of the Monograph Review Committee of the Solid Waste Processing Division, the Hazardous Waste Committee of the Environmental Engineering Division, and the Research Committee on Industrial and Municipal Waste, each with technical expertise and interest in the field covered by this document. Although, as indicated on the reverse of the title page of this document, neither ASME nor any of its Divisions or Committees endorses or recommends, or makes any representation or warranty with respect to, this document, those Divisions and Committees which conducted a review believe, based upon such review, that this document and findings expressed are technically sound.

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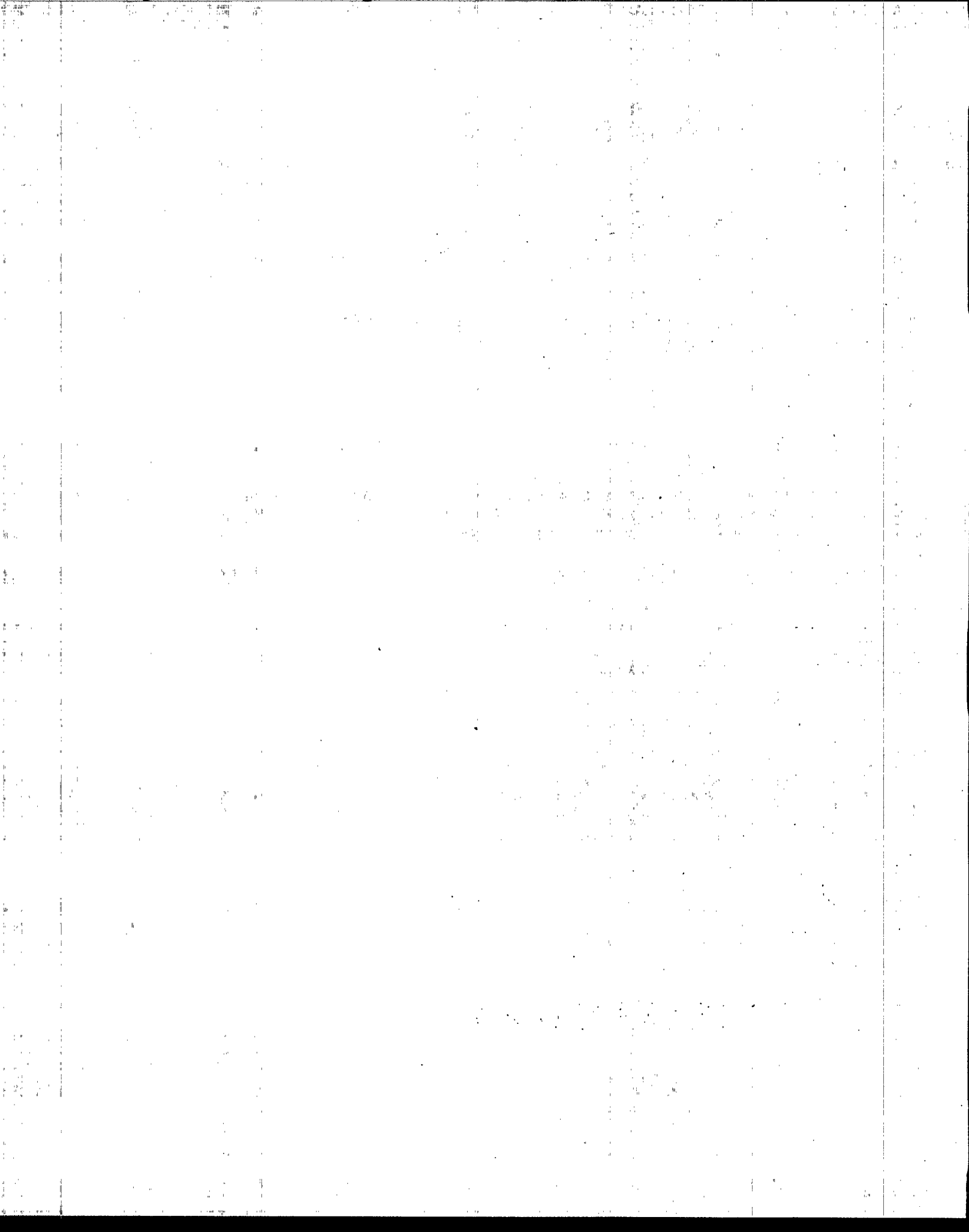
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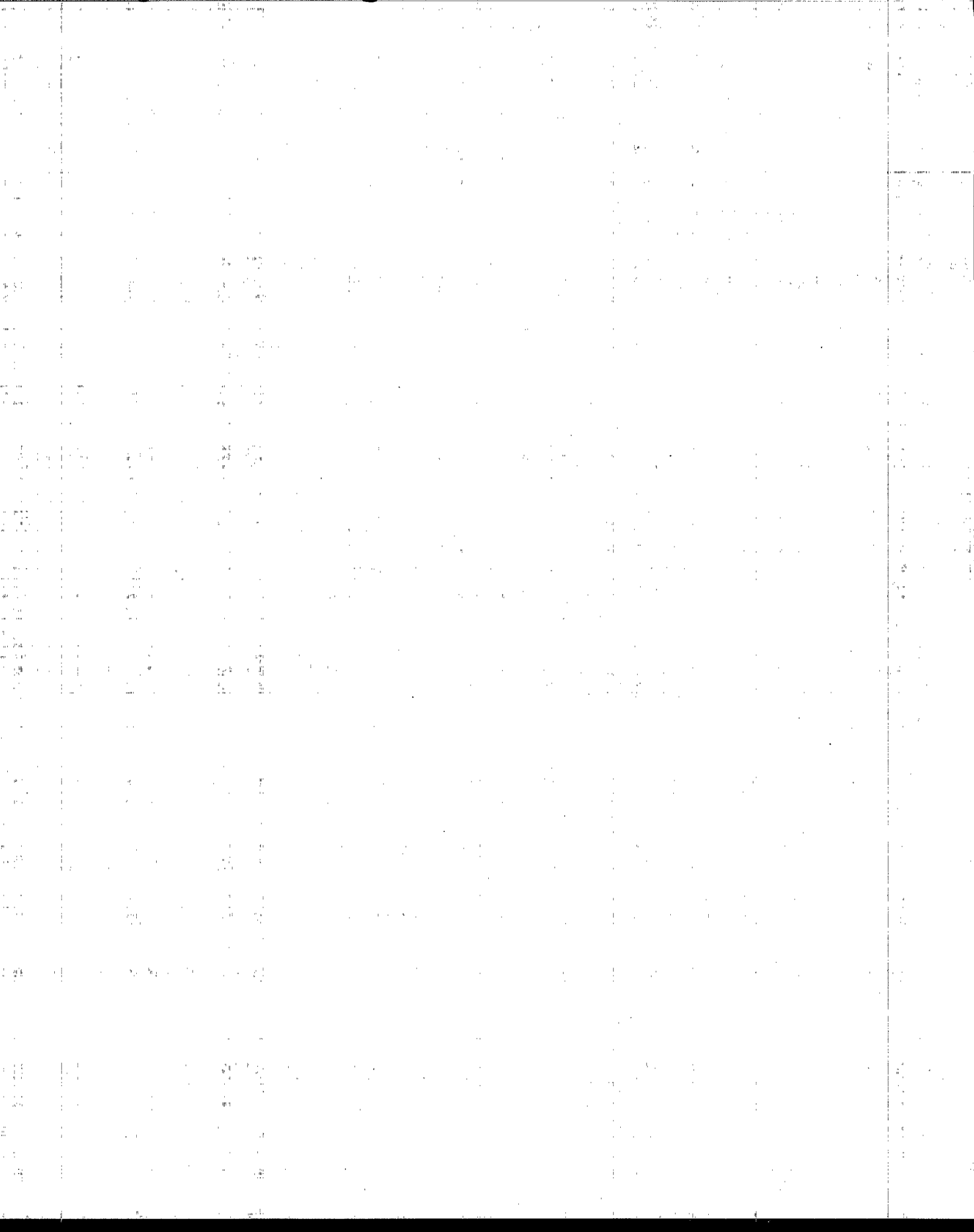
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# INTRODUCTION

This monograph covering the *design, applications, and implementation* of selected Thermal Destruction technologies, is one of a series of seven on innovative site and waste remediation technologies. This series of seven was preceded by eight volumes published in 1994 and 1995 covering the description, evaluation, and limitations of the processes. The entire project is the culmination of a multi-organization effort involving more than 100 experts. It provides the experienced, practicing professional with guidance on the innovative processes considered ready for full-scale application. Other monographs in this design and application series and the companion series address bioremediation; chemical treatment; liquid extraction; soil washing, soil flushing, and solvent/chemical extraction; stabilization/solidification; thermal desorption; and vapor extraction and air sparging.

## 1.1 Thermal Destruction

Thermal destruction, as considered in this monograph, is an ex-situ process that thermally destroys organic contaminants. Often, thermal destruction is considered a mature technology employing a variety of reaction chambers. Rotary kilns are most common. Innovation in this area has occurred primarily in the form of modifications and improvements to existing systems, process reactions, and by-products.

Information on the more established thermal destruction technologies used in site remediation can be found in the companion monograph, *Innovative Site Remediation Technology — Thermal Destruction* (Magee et al. 1994). Thermal destruction technologies discussed in that monograph include: catalytic oxidation, rotary cascading bed incineration, the ECO LOGIC thermo-chemical reduction reactor, and the HRD flame reactor process.

This monograph on design and application focuses on wet air oxidation, the Texaco gasification process, flameless thermal oxidation, and plasma furnaces. Two of these processes, wet air oxidation and flameless thermal oxidation, are useful adjuncts to treating by-products from other remediation technologies.

## ***1.2 Development of the Monograph***

### **1.2.1 Background**

Acting upon its commitment to develop innovative treatment technologies for the remediation of hazardous waste sites and contaminated soils and groundwater, the U.S. Environmental Protection Agency (US EPA) established the Technology Innovation Office (TIO) in the Office of Solid Waste and Emergency Response in March, 1990. The mission assigned TIO was to foster greater use of innovative technologies.

In October of that same year, TIO, in conjunction with the National Advisory Council on Environmental Policy and Technology (NACEPT), convened a workshop for representatives of consulting engineering firms, professional societies, research organizations, and state agencies involved in remediation. The workshop focused on defining the barriers that were impeding the application of innovative technologies in site remediation projects. One of the major impediments identified was the lack of reliable data on the performance, design parameters, and costs of innovative processes.

The need for reliable information led TIO to approach the American Academy of Environmental Engineers®. The Academy is a long-standing, multi-disciplinary environmental engineering professional society with wide-ranging affiliations with the remediation and waste treatment professional communities. By June 1991, an agreement in principle (later formalized as a Cooperative Agreement) was reached providing for the Academy to manage a project to develop monographs providing reliable data that would be broadly recognized and accepted by the professional community, thereby eliminating or at least minimizing this impediment to the use of innovative technologies.

The Academy's strategy for achieving the goal was founded on a multi-organization effort, WASTECH® (pronounced Waste Tech), which joined in partnership the Air and Waste Management Association, the American Institute of Chemical Engineers, the American Society of Civil Engineers, the American Society of Mechanical Engineers, the Hazardous Waste Action Coalition, the Society for Industrial Microbiology, the Soil Science Society of America, and the Water Environment Federation, together with the Academy, US EPA, DoD, and DOE. A Steering Committee composed of highly-respected representatives of these organizations having expertise in remediation technology formulated the specific project objectives and process for developing the monographs (see page iv for a listing of Steering Committee members).

By the end of 1991, the Steering Committee had organized the Project. Preparation of the initial monographs began in earnest in January, 1992, and the original eight monographs were published during the period of November, 1993, through April, 1995. In Spring of 1995, based upon the reception by the industry and others of the original monographs, it was determined that a companion set, emphasizing the design and application of the technologies, should be prepared as well. Task Groups were identified during the latter months of 1995 and work commenced on this second series.

### 1.2.2 Process

For each of the series, the Steering Committee decided upon the technologies, or technological areas, to be covered by each monograph, the monographs' general scope, and the process for their development. The Steering Committee then appointed a task group composed of experts to write a manuscript for each monograph. The task groups were appointed with a view to balancing the interests of the groups principally concerned with the application of innovative site and waste remediation technologies — industry, consulting engineers, research, academia, and government.

The Steering Committee called upon the task groups to examine and analyze all pertinent information available within the Project's financial and time constraints. This included, but was not limited to, the comprehensive data on remediation technologies compiled by US EPA, the store of information possessed by the task groups' members, that of other experts willing to voluntarily contribute their knowledge, and information supplied by process vendors.

To develop broad, consensus-based monographs, the Steering Committee prescribed a twofold peer review of the first drafts. One review was conducted by the Steering Committee itself, employing panels consisting of two members of the Committee supplemented by other experts (See *Reviewers*, page iii, for the panel that reviewed this monograph). Simultaneous with the Steering Committee's review, each of the professional and technical organizations represented in the Project reviewed those monographs addressing technologies in which it has substantial interest and competence.

Comments resulting from both reviews were considered by the task group, appropriate adjustments were made, and a second draft published. The second draft was accepted by the Steering Committee and participating organizations. The statements of the organizations that formally reviewed this monograph are presented under *Reviewing Organizations* on page v.

### **1.3 Purpose**

The purpose of this monograph is to further the use of innovative thermal destruction site remediation and waste processing technologies, that is, technologies not commonly applied; where their use can provide better, more cost-effective performance than conventional methods. To this end, the monograph documents the current state of thermal destruction technology.

### **1.4 Objectives**

The monograph's principal objective is to furnish guidance for experienced, practicing professionals and users' project managers. This monograph, and its companion monograph, are intended, therefore, not to be prescriptive, but supportive. It is intended to aid experienced professionals in applying their judgment in deciding whether and how to apply the technologies addressed under the particular circumstances confronted.

In addition, the monograph is intended to inform regulatory agency personnel and the public about the conditions under which the processes it addresses are potentially applicable.

## **1.5 Scope**

The monograph addresses innovative thermal destruction technologies that have been sufficiently developed so that they can be used in full-scale applications. It addresses all aspects of the technologies for which sufficient data were available to the Thermal Destruction Task Group to briefly review the technologies and discuss their design and applications.

The monograph's primary focus is site remediation and waste treatment. To the extent the information provided can also be applied elsewhere, it will provide the profession and users this additional benefit.

Application of site remediation and waste treatment technology is site-specific and involves consideration of a number of matters besides alternative technologies. Among them are the following that are addressed only to the extent that they are essential to understand the applications and limitations of the technologies described:

- site investigations and assessments;
- planning, management, and procurement;
- regulatory requirements; and
- community acceptance of the technology.

## **1.6 Limitations**

The information presented in this monograph has been prepared in accordance with generally recognized engineering principles and practices and is for general information only. This information should not be used without first securing competent advice with respect to its suitability for any general or specific application.

Readers are cautioned that the information presented is that which was generally available during the period when the monograph was prepared. Development of innovative site remediation and waste treatment technologies is ongoing. Accordingly, post-publication information may amplify, alter, or render obsolete the information about the processes addressed.

This monograph is not intended to be and should not be construed as a standard of any of the organizations associated with the WASTECH® Project; nor does reference in this publication to any specific method, product, process, or service constitute or imply an endorsement, recommendation, or warranty thereof.

### ***1.7 Organization***

This monograph and others in the series are organized under a similar outline intended to facilitate cross reference among them and comparison of the technologies they address.

Chapter 2, Application Concepts, summarizes the process, its scientific basis, the potential applications, and key requirements for thermal destruction technologies. Design Development, Chapter 3, provides essential information for those contemplating use of the technologies discussed. Chapter 4, Implementation and Operation, focuses on the procedures commonly used to implement thermal destruction technologies and key facets of their operation. Finally, Chapter 5 presents example case histories.





## APPLICATION CONCEPTS

Thermal destruction, as considered in this monograph, is an ex-situ process that destroys or removes organic compounds or metals from contaminated matrices. The reader is referred to the companion monograph, *Innovative Site Remediation Technology — Thermal Destruction* (Magee et al. 1994) for information on other more established technologies, specifically, catalytic oxidation, rotary cascading bed incineration, the ECO LOGIC thermo-chemical reduction reactor, and the HRD flame reactor process. This monograph on design and application focuses on wet air oxidation, the Texaco Gasification Process, flameless thermal oxidation, and plasma furnaces. Two of these processes, wet air oxidation and flameless thermal oxidation, are useful adjuncts to treating by-products from other remediation technologies.

### 2.1 Wet Air Oxidation

#### 2.1.1 Scientific Principles

Wet Air Oxidation (WAO) is a process for oxidizing materials in a dilute aqueous matrix. The process has been applied industrially to detoxify organic and, to a lesser extent, oxidizable inorganic materials in dilute solution or suspension. High destruction efficiencies (99+%) have been reported for a wide range of materials. The process substantially reduces chemical oxygen demand (COD); the COD of the product is usually 25% or less than that of the original waste stream. Typically, biological treatment is used as a final polishing step.

The major WAO system suppliers are U.S. Filter-Zimpro, Kenox Corporation, and Nippon Petrochemical. Table 2.1, a listing of recent WAO

**Table 2.1**  
Recent WAO Installations

Installation	Application	# of Units	Capacity (gal/min)	Start-up Date
Yukong Ltd. Ulsan, S. Korea	Spent Caustic	1	145	1989
CPC-Kaohsiung Refinery	Spent Caustic	3	25	1990
Quantum Chemical Deer Park, TX	Spent Caustic	1	21	1991
Finaneste Antwerp, Belgium	Spent Caustic	1	25	1991
Westlake Polymer Lake Charles, LA	Spent Caustic	1	10	1991
CPC-Talin Refinery	Spent Caustic	3	53	1994
Formosa Plastics Point Comfort, TX	Spent Caustic	1	21	1994
Sterling Organics Dudley, UK	Pharmaceutical	1	30	1992
Yorkshire Water Leeds, UK	Commercial Treatment	1	10	1993
Phillips Petroleum Sweeny, TX	Spent Caustic	1	66	1993
CPC-Lin Yuan Refinery	Spent Caustic	2	17	1994
BLEME Petrochemicals Co. Port Harcourt, Nigeria	Spent Caustic	1	35	UC
Refinaria de Petroleos de Manguinhos Rio de Janeiro	Spent Caustic	1	25	UC

UC Under construction

Source: Momont, Copa, and Randall 1995

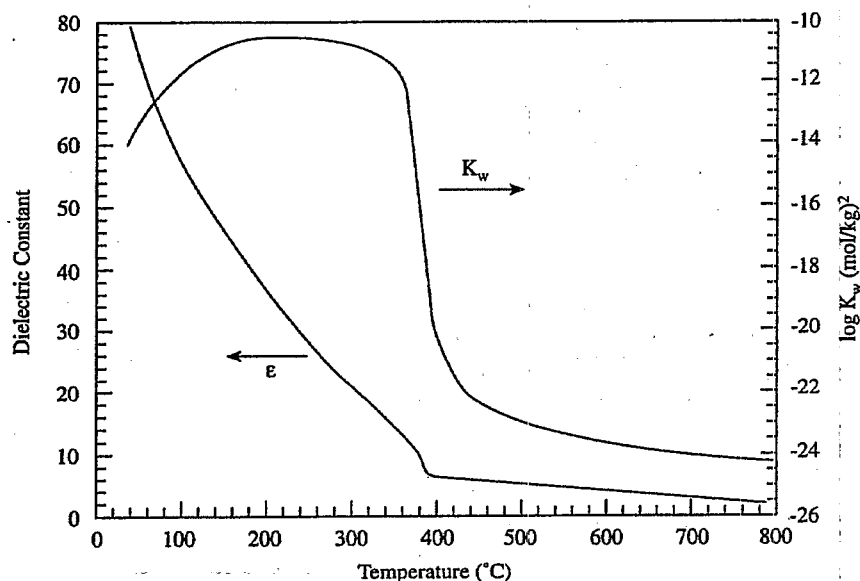
installations (Momont, Copa, and Randall 1995), shows a large number of applications for treating spent caustic wastes.

To maintain a liquid phase in the usual operating temperature range of 150 to 320°C (300 to 600°F), pressure must be in the range from 0.5 to 11.5 MPa (75 to 1,700 lb/in.<sup>2</sup>). The high pressure necessary for the process is

usually generated by pumping and compressing. An interesting alternative is to drill a deep hole and pump water and reactants down (and back up) via concentric piping; the column of liquid provides the high pressure required at the bottom of the hole. However, this discussion of WAO is devoted to the more usual, aboveground technology, although the chemistry and scientific principles apply to both methods. Mishra, Vijaykumer, and Joshi (1995) have extensively reviewed research work on the WAO process.

The properties of water change as temperature (and pressure) increase. At room temperature water is a highly polar fluid; nonpolar materials (e.g., hydrocarbons) are almost insoluble, while most salts have high solubilities. Under usual WAO conditions, the fluid properties (solubility characteristics in particular), still resemble those of ordinary water, as shown in Figure 2.1.

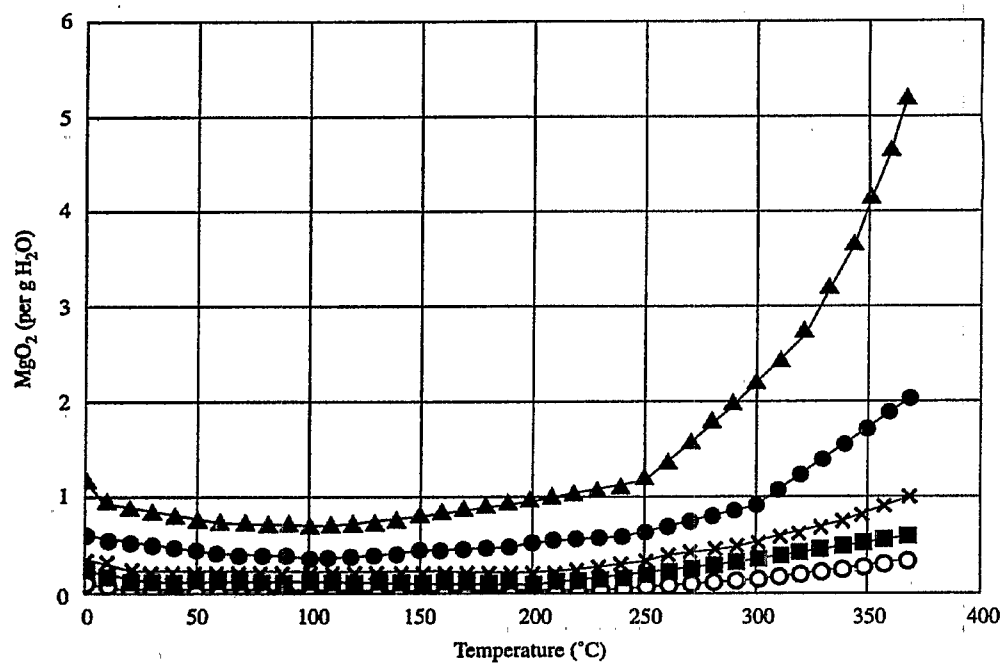
**Figure 2.1**  
Solvation Properties of Pure Water (at 25 MPa)



Source: Copa 1995

The solubility of oxygen is also important to the process (Figure 2.2). Under normal conditions for WAO, the solubility remains well below that required for most applications; oxygen must continue to be transferred from the gas to the liquid phase to complete the oxidation. It is worth noting that supercritical water oxidation is covered under *Chemical Treatment* in this series of monographs.

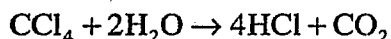
**Figure 2.2**  
Oxygen Solubility In Water



○ 10 PSIA  $\text{P}(\text{O}_2)$   
■ 25 PSIA  
× 50 PSIA  
● 100 PSIA  
▲ 250 PSIA

Source: Copa 1995

Water at high temperature and pressure, approaching critical conditions, will react with most organic materials even in the absence of oxygen. The hydrolysis of carbon tetrachloride at elevated temperature and pressure is known to produce hydrochloric acid and carbon dioxide:



Other halogenated organic compounds hydrolyze to alcohols and carbonyl compounds (Copa 1995).

Most, if not all, organic compounds are attacked under WAO conditions. Typical products, in addition to carbon dioxide and water, are a small amount of carbon monoxide, soluble carbonate and bicarbonate, and acetic acid, acetone, butanone, and other low molecular weight oxygenated materials. Elements, such as halogens, nitrogen, phosphorous, sulfur, are usually released as halides, ammonia, or other nitrogen gases, phosphate, and sulfate; these elements are separated almost completely from the residual organics (Momont, Copa, and Randall 1995).

Many different materials, including  $\text{Cu}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{CuO/ZnO}$ ,  $\text{Cu}^{3+}$ , and  $\text{Ce}^{4+}$  will catalyze the oxidation reactions. Homogeneous and heterogeneous catalyses have been used experimentally. The presence of catalyst in the liquid discharge complicates the final disposition, particularly for a soluble homogeneous catalyst. Catalysis does not appear to have been used in industrial systems.

Wet air oxidation has been studied in considerable detail for a few types of chemicals using small-scale, batch reactors. Carboxylic acids have been studied because of their importance as intermediates in the oxidation process. Phenols and some nitrogen compounds (cyanides and nitriles) have also been studied because of their prevalence and hazardous properties. In addition, many and varied materials have been tested for completeness of reaction, etc. Such work has been done in both batch and flow-through type reactors, much of it to provide information for plant design.

The oxidation reactions usually progress in a series of steps involving free radicals (Sadana and Katzer 1974). As a result, the detailed kinetics are complicated with a variety of reaction orders being reported for different materials.

### 2.1.1.1 Carboxylic Acids

Long chain molecules are broken down quickly to intermediates which then react more slowly. The effluent products can be divided into three groups: remaining unstable (initial) intermediates, refractory intermediates such as acetic acid, and endproducts, such as carbon dioxide or carbonates.

The results of most of the studies have been summarized by Mishra, Vijaykumar, and Joshi (1995). Linear monocarboxylic acids (formic, acetic, propionic, butyric, valeric, and caproic), and dicarboxylic acids (oxalic, adipic, succinic, and glutaric) were studied. In summary, reaction rates were found to be on the order of 1.0 to 1.5 with respect to the substrate concentrations; the order with respect to oxygen pressure was generally in the range 0.31 to 0.46 (although one reference reported an order close to zero). Activation energies were reported in the range 75 to 142 kJ/mole. The reaction rate generally increased with size of the molecule (formic acid is an exception; it is easily oxidized), and dibasic acids were more readily oxidized than monobasic acids. The extent of reaction for most of the materials studied was low to moderate, illustrating the fact that low molecular weight acids are refractory and tend to show up in the effluent products. Inamura, Kinunaka, and Kawabata (1982) illustrate this with the data shown in Table 2.2 from a catalyzed system. Experience also indicates the same trends in uncatalyzed systems.

### 2.1.1.2 Phenol and Substituted Phenols

A particularly interesting observation is that WAO of most phenols exhibits a pronounced induction period, the length of which depends on the severity of the oxidation conditions (i.e., temperature and pressure), as well as the particular phenol. The induction period is presumably related to establishing a reactive concentration of an important chain carrier. This has been examined in some detail by Sadana and Katzer (1974).

The oxidation process for phenols occurs at variable rates due to the presence of side chains; alkyl side chains oxidize much more readily than the ring, resulting in rapid formation of radicals. Therefore, the oxidation shows a rapid initial rate as the alkyl groups are oxidized, followed by a slower reaction as the ring is broken down.

Studies done at relatively low temperature (25 to 80°C [77 to 176°F]) have identified some very reactive intermediates in the oxidation process, e.g., pyrocatechol and hydroquinone, as well as carboxylic acids. Some

**Table 2.2**  
Removal of Carboxylic Acids by WAO

Substrate	Temperature (°C)	Total Organic Carbon (% Removal)
Formic Acid	112	17.3
Acetic	248	8.3
Propionic	248	6.9
Butyric	248	17.5
Valeric	248	8.3
Hexanoic	248	12.4
Oxalic	160	90.0
Adipic	248	27.3
Succinic	248	58.6
Glutamic	248	72.5

WAO at  $P_{O_2}$  = 1 MPa  
Time = 20 min

Note: Total system pressure is much higher than the oxygen partial pressure of 1 MPa (145 lb/in.<sup>2</sup>).

Source: Imamura, Kinunaka, and Kawabata 1982

polymeric material, tars, might also form, although these are not observed at normal (higher temperature) conditions.

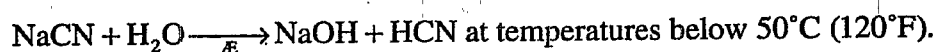
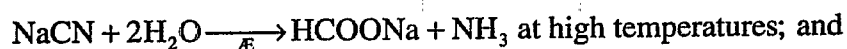
The reaction orders for phenol oxidation are similar to those for carboxylic acid — first order for the substrate and low (approaching zero) for oxygen. The activation energies reported are lower, 5.44 to 54.01 kJ/mol (Mishra, Vijaykumer, and Joshi 1995).

### 2.1.1.3 Cyanides and Nitriles

Nitrogen-containing compounds can react to yield various products:  $N_2$ ,  $NH_3$ ,  $CN^-$  (Mishra, Vijaykumer, and Joshi 1995). Hydrolysis appears to be an important first step in the WAO of both cyanides and nitriles. Thus, acrylonitrile is reported to undergo hydrolysis to acrylamide and then to acrylic

acid (liberating  $\text{NH}_3$ ), followed by oxidation of the acid. The oxidation of the acid is the slow step.

Cyanide can be hydrolyzed, depending on temperature:



$\text{NaCN}$  can also be oxidized directly, first to give cyanate and then nitrogen. Thus, oxidation of cyanides can yield both  $\text{N}_2$  and  $\text{NH}_3$  (the latter being resistant to further oxidation).

A range of reaction orders and activation energies for nitrogen-compounds have been reported; see Mishra, Vijaykumer, and Joshi (1995) for details.

### 2.1.2 Potential Applications

Patents for WAO technology date back to 1911 — however, industrial application has occurred mainly in the past 25 years. The extension of the concept to supercritical conditions has spurred interest.

Wet air oxidation is a versatile process which might have advantages over competing technologies where the following conditions prevail:

- the feed material to be oxidized is in the form of a fairly dilute, aqueous solution or suspension — usually in the range of 1 to 5% solids;
- biological treatment of the feed material is either ineffective or inconvenient because of limited space or other considerations; and
- the moderate to high pressure requirement for WAO treatment is not viewed as a serious safety hazard.

More than 200 WAO plants have been built worldwide. The applications fall into two principal categories:

- Roughly half of the applications have been used to treat sewage sludges, consisting of low concentrations of sewage in water, typically less than 2%. The process conditions are mild so that only a modest amount of oxidation occurs, e.g., 15% reduction in COD. The products are (1) a liquid effluent containing partially



oxidized organic matter and most of the original sulfur content present as sulfate; and (2) a solid residue that is easily dewatered and either incinerated or, in some cases, landfilled when sufficiently stable and detoxified.

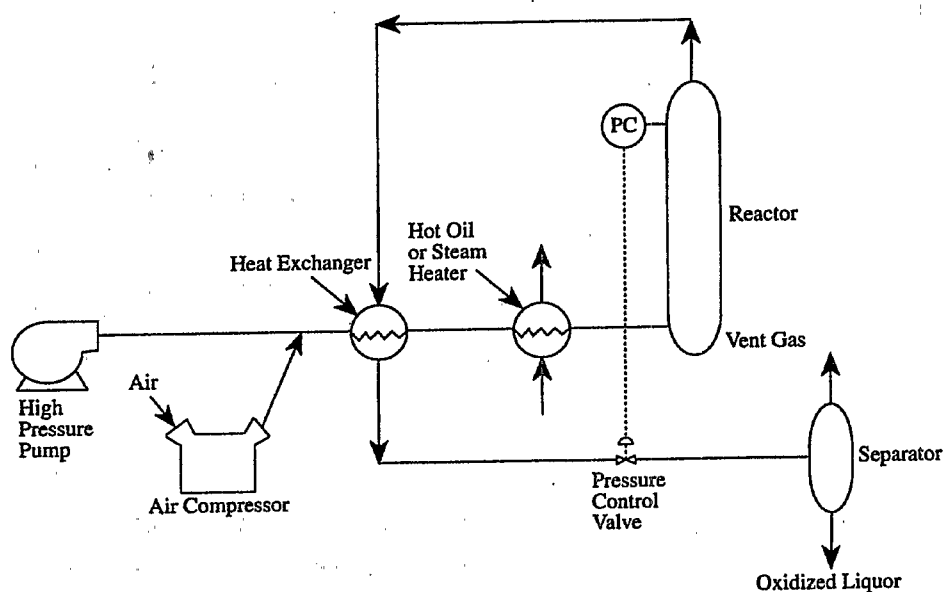
- The other applications have been to a wide variety of waste solutions at low concentrations — less than 2% — from the chemical, petroleum, pharmaceutical, and metallurgy industries. In most cases, the materials were not suitable for direct biological treatment and their high water content made them difficult to detoxify by other methods, such as direct incineration.

A flow plan for a continuous WAO process is shown in Figure 2.3. The oxidation process generates heat so that the temperature rises in the reactor to the final desired temperature. The flow diagram shown applies to a very dilute feed which would release too little heat to achieve the desired temperature. Therefore, additional heat is added. With higher concentration feeds, the reverse may be true; heat must be removed by cooling or by generating high pressure steam. Typically, the process can operate with no additional energy if the oxygen uptake is greater than 15 g/L. Air is the oxidizing gas normally used, though enrichment with oxygen has been used and has reduced costs in some cases. Plants have been designed for pure oxygen, but none are in operation. The process resembles combustion in that it is generally applicable to combustible organics. The high pressure is an obvious disadvantage, particularly with very toxic materials, where any accidental release could be harmful; some preliminary chemical detoxification could be considered for such cases.

Most applications have been to organic materials; the process is also applicable to oxidizable inorganic materials, although there have been only a few applications to date.

The WAO process is capable of a high degree of conversion of toxic organics, e.g., 99+% conversion. Most materials, however, are not oxidized completely to final oxidation states,  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ , etc. Instead, the reaction proceeds through a series of intermediate compounds and some of these are slow to oxidize further. For example, some carboxylic acids — acetic acid in particular — remain in solution and can represent 25% of the original weight of organic. The usual WAO process is followed by biological treatment of the liquid.

**Figure 2.3**  
WAO Flow Diagram



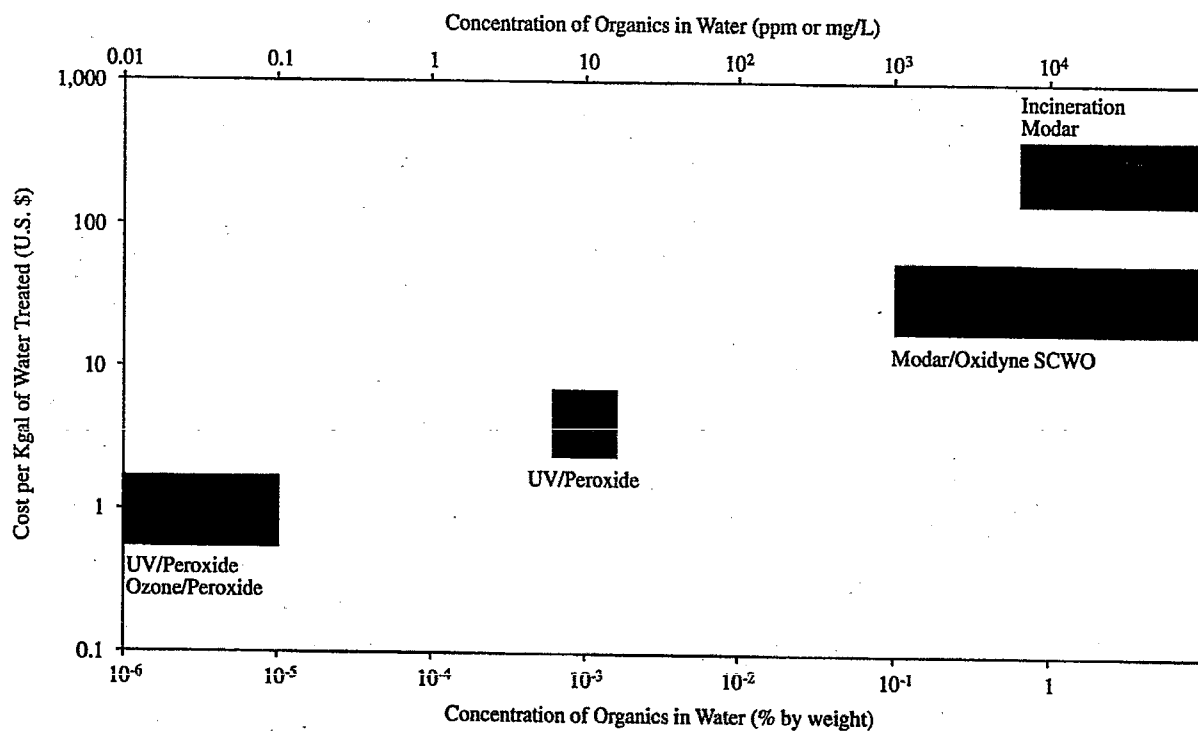
Source: Copa and Lehmann 1992

As indicated previously, the process conditions call for a rather low concentration of oxidizable material in water. Unit treatment costs (i.e., the cost to oxidize a pound of organics) generally increase with greater dilution (see Figure 2.4).

Consequently, WAO would appear to be particularly suitable for highly dilute wastes. The process could find application to toxic materials in highly concentrated or energetic form; in this case, dilution is necessary and additional costs are incurred.

The material to be oxidized does not need to be completely miscible with water. Partly miscible liquids and solids can be treated. However, they must be finely dispersed so that they do not settle out in the reactor.

**Figure 2.4**  
Projected Costs of Advanced Oxidation Processes for Destruction of Organic Contaminants in Water



Source: Glaze 1991

Products of the oxidation process have (at least to date) been soluble under the reactor conditions; no problems have been encountered with insoluble salts or other products settling out in the reactor or in the expansion valves.

### 2.1.3 Treatment Trains

Posttreatment of the products from WAO is generally required and pretreatment is sometimes desirable. Feed materials containing species such as chlorine, can yield very acidic conditions upon oxidation. Caustic addition to the feed might be necessary for corrosion control. The vent gas shown in Figure 2.3, consisting primarily of depleted air and carbon dioxide, can contain part per million levels of carbon monoxide and low molecular weight organics which might require a catalytic oxidation step before release.

The oxidized liquor shown in Figure 2.3 generally is treated in a biological processing plant where the low molecular weight organics in solution are readily converted. Inorganic salts in the process liquor might require recovery (by evaporation) and land filling if concentrations are high.

## 2.2 *Texaco Gasification Process*

### 2.2.1 Scientific Principles

This process reacts organic compounds with steam and oxygen to form a mixture of carbon monoxide, carbon dioxide, and hydrogen. Depending on feed composition, there may also be products of reaction of chlorine, nitrogen, sulfur, and other elements that form volatile compounds in a hydrogen-rich atmosphere under high temperature conditions. Low volatility inorganic components of the feed are converted to molten slag and some fines that leave the reactor with the gas stream.

The major reactions for carbon are:



The first of these reactions is exothermic and provides the major source of heat needed to run the process. This heat is used to bring the feed to reaction temperature and to supply heat for the second reaction which is highly endothermic. Low heating value feedstocks (the waste materials) must be supplemented with coal or another high heating value feedstock to achieve the required operating temperature in the reactor.

### 2.2.2 Potential Applications

The Texaco Gasification Process (TGP) is used in the petroleum and chemical industries to produce hydrogen and synthesis gas — also known as syngas, a mixture of  $H_2$ ,  $CO$ , and  $CO_2$  — from tars and coal. Virtually any carbonaceous, hazardous, or nonhazardous waste stream can be processed in the TGP as long as adequate facilities are provided for pretreatment and storage. The TGP has operated commercially for nearly 45 years on feeds such as natural gas and coal, and nonhazardous wastes, such as liquid petroleum fractions and petroleum coke (US EPA 1995).

Depending upon the physical and chemical composition of the waste stream, it can either be used as the primary feed to the gasifier, or it can be co-gasified with a high-Btu fuel, such as coal, petroleum, coke, or oil. The combined feed must be slurried successfully, high enough in heating value to maintain gasifier temperatures, and composed of an ash matrix with a fusion temperature that falls within operational limits (US EPA 1995).

In general, the ratio of waste feed to fuel can be adjusted over a wide range. Although a waste stream can serve as the sole feed to the gasifier, blending the waste with another feed can ensure continuity and stability of operation. The TGP can treat wastes that fall into three categories (US EPA 1995):

- solid or liquid wastes that contain sufficient energy to sustain gasifier operation as the sole feed without adding another higher-heating-value fuel;
- solid wastes with heating values too low to sustain gasifier operation that can be supplemented with a higher-heating-value fuel, such as coal; and
- liquid waste with insufficient heating values that can be combined with a higher-heating-value fuel. In this case, the liquid waste can be used as the fluid phase of the primary feed slurry.

Texaco's gasification process is currently licensed in the U.S. and abroad. The syngas is used for the production of electric power and numerous chemical products, such as ammonia, methanol, and high-purity hydrogen. As an innovative process gasifying less traditional and hazardous wastes, Texaco reports that the TGP has processed various waste matrices containing a broad range of hydrocarbon compounds, including coal liquefaction residues, California hazardous waste material from an oil production field (petroleum production tank bottoms), municipal sewage sludge, waste oil, used automobile tires, waste plastics, and low-Btu soil. Texaco licensees in Europe have had long-term success in gasifying small quantities of hazardous waste as supplemental feedstock, including PCBs, chlorinated hydrocarbons, styrene distillation bottoms, and waste motor oil (US EPA 1995).

It was also used in California to demonstrate production of electric power from coal for the Cool Water Program (Electric Power Research Institute 1993). Here, the medium-Btu fuel gas produced was cleaned and burned in a gas-fired power plant. The low price and ready availability of natural gas made use of coal uneconomical, and the gasifier has since been used to produce synthetic natural gas and electricity from a sewage sludge/coal mixture.

Texaco expects to design TGP facilities with flexible and comprehensive storage and pretreatment systems capable of processing a wide range of waste matrices slurried with coal or oil, water, and additives (US EPA 1995). Although commercial gasification units are much larger than typical waste disposal units, a transportable, 91 tonne/day (100 ton/day) unit has been proposed for use at large waste sites. Texaco has also announced plans to build a \$75 million gasification facility at their El Dorado, Kansas, facility which will process about 150 tonne/day (170 ton/day) of noncommercial petroleum coke and refinery wastes into fuel gas for internal use. The syngas, combined with natural gas, will power a gas turbine to produce approximately 40 MW (54,000 hp) of electrical power — enough to meet the full needs of the refinery. The exhaust heat from the turbine will produce 82,000 kg/hr (180,000 lb/hr) of steam — approximately 40% of the refineries' requirements. Startup is projected for the second quarter of 1996.

The TGP can process all waste stream matrices based on the availability of adequate materials — handling, pretreatment, and slurrying equipment. The unit's complexity and costs, and the economic benefit of a tie-in to its syngas product, mandate that on-site remediations be limited to relatively large sites with a minimum of approximately 45,000 tonne (50,000 ton) of

waste feed and about two years of operation (US EPA 1995). Alternatively, smaller amounts of waste could be transported to an industrial facility.

### 2.2.3 Treatment Trains

Figure 2.5 presents a schematic diagram of the process. Liquid and gaseous feeds can be injected directly into the reactor. Solid feeds, which might first require grinding and sieving, are mixed with water to form a pumpable slurry that is injected along with oxygen into the top of the reaction chamber where the temperature is typically  $1,480^{\circ}\text{C}$  ( $2,700^{\circ}\text{F}$ ) and the pressure 4 MPa ( $600\text{ lb/in.}^2$ ). This mixture ignites and flows downward through the reactor with a residence time of a few seconds. The molten slag is cooled and solidified by water injection and, in some cases, radiant cooling.

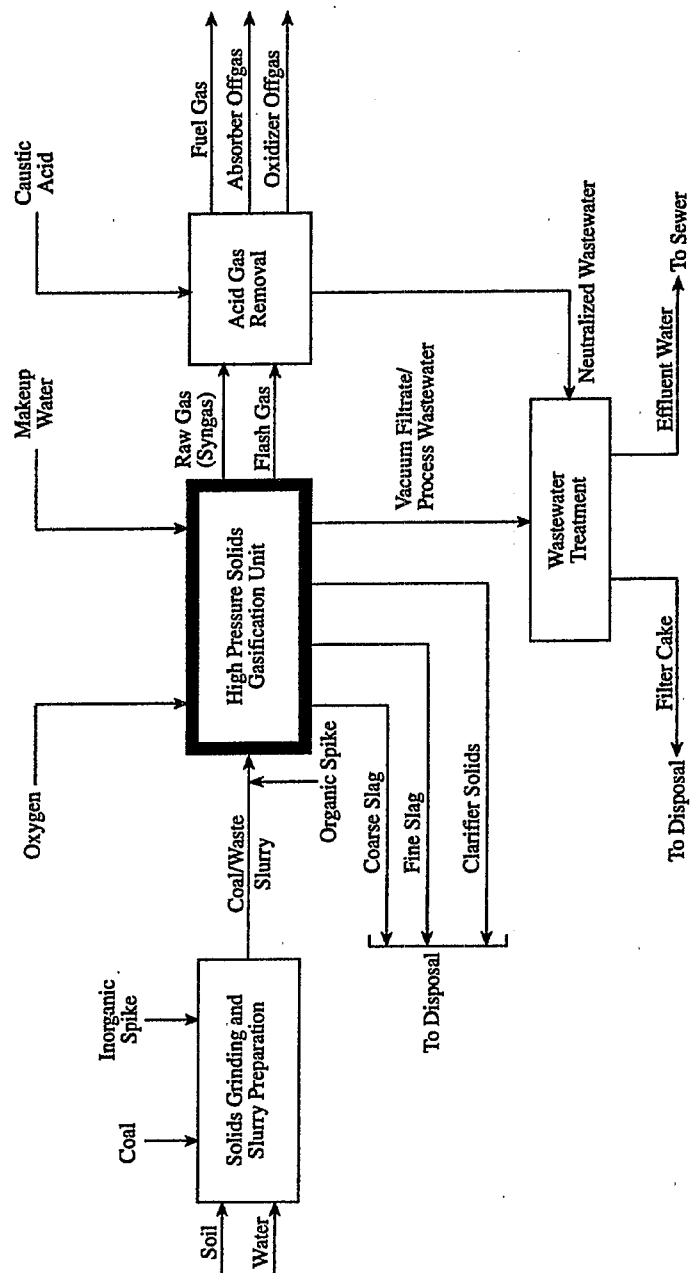
Approximately two-thirds of this solidified slag is classified as coarse and can then be used for fill, aggregate, or sent to a landfill disposal site. The fine particles are combined with fines from the gas cleanup system and either recycled to the reactor or disposed directly. The gaseous stream is then cooled and treated to remove particulates and other impurities (DOE 1987).

## 2.3 Flameless Thermal Oxidation

### 2.3.1 Scientific Principles

Flameless thermal oxidation is a patented technology being developed and marketed by Thermatrix, Incorporated. The basic process consists of thoroughly mixing and then heating a gas which contains organic contaminants to temperatures at which oxidation occurs under very uniform, stable conditions. These stable conditions are obtained by passing the contaminated gas stream through a packed bed of hot, chemically inert, ceramic materials that thoroughly mix and heat the incoming gases to reaction temperatures and absorb a portion of the heat released during oxidation (Binder and Martin 1993). The oxidation of the organics is flameless and occurs at concentrations below the lower explosive limit (LEL). The highly visible, high temperature flame front that normally exists during the combustion of flammable gases in a burner is not present in the Thermatrix unit. There are

**Figure 2.5**  
Block-Flow Diagram of the Texaco Gasification Process





two major equipment related differences between the Thermatrix design and a conventional flame burner-based, fume incinerator: (1) the Thermatrix flameless thermal oxidizer (FTO) uses a reaction chamber containing ceramic packing instead of an empty chamber, and (2) it does not use a burner flame for heat transfer to the vent gas.

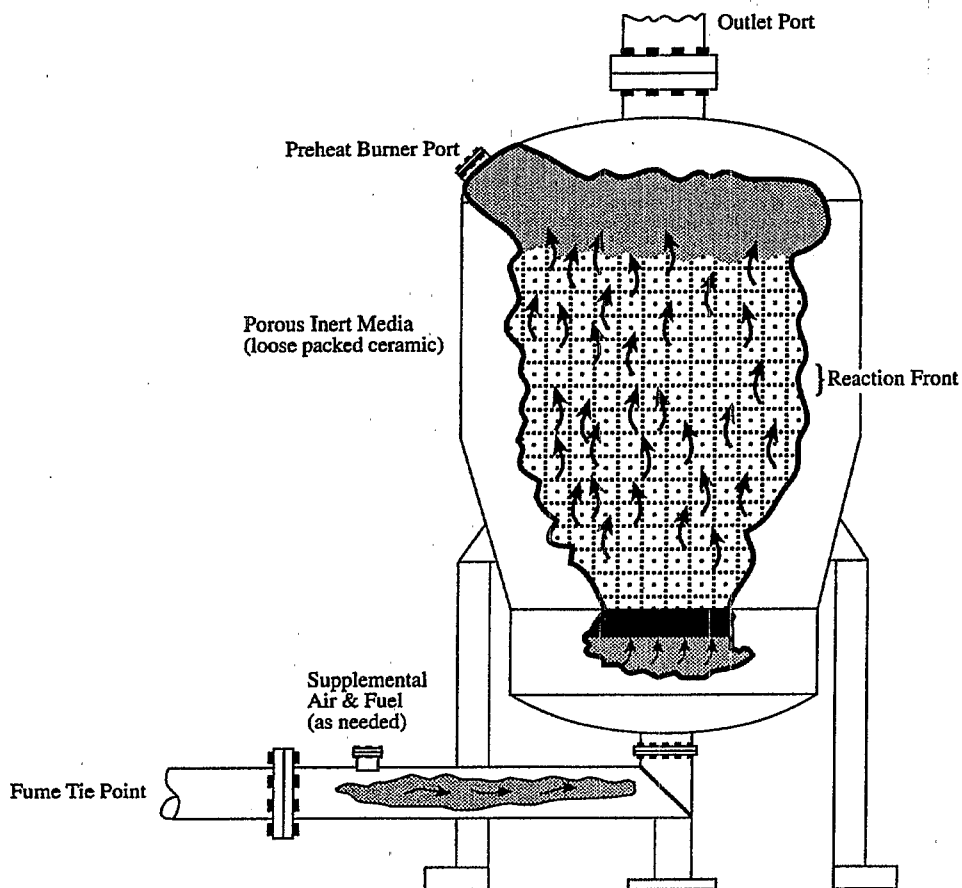
One configuration for the FTO is shown in Figure 2.6. In this design, the contaminated gas enters the distribution plenum through the inlet port, flows upward into the mixing zone, which is at ambient temperature, and then goes to the reaction zone, which is maintained at high temperatures — typically in the 870 to 1,010°C (1,600 to 1,850°F) range (Wilbourn, Allen, and Baldwin 1995). The mixing and reaction zones are packed with different types of ceramic media. After mixing, the contaminated gas enters the reaction zone. As the contaminated gas flows through the reaction zone, it is heated by the hot ceramic packing to the oxidation temperature. At some point in the reaction zone, a relatively uniform and stationary reaction wave is formed perpendicular to the axis of gas flow throughout a cross-section of the reaction zone. The oxidation taking place in the reaction wave between the organics and oxygen releases energy back to the ceramic matrix, replacing some or all of the energy used to heat the gas to the oxidation temperature (Binder and Martin 1993).

The amount of air used can be automatically adjusted based on organic concentration. If the waste stream has a low organic concentration, which is unable to support oxidation and maintain the matrix at operating temperature, thermal energy can be introduced by using an electric heating element or an internal heat recuperation system, or by adding natural gas or propane to the contaminated gas in the distribution plenum (Wilbourn, Allen, and Baldwin 1995).

The ceramic packing in both the mixing and reaction zones ensures mixing of oxygen and the contaminated gas and a very even axial temperature distribution in the bed. Because the reaction wave covers the entire flow cross-section of the reactor, all organic constituents present in the contaminated gas pass through this reactive region. The reaction wave contains active radicals that cause the oxidation reaction in the reaction wave to occur at higher rates than would occur in the post-flame region of a conventional flame-fired fume incinerator (Binder and Martin 1993). Residence times of 0.2 sec are sufficient to achieve high destruction efficiencies (DeCicco 1996). The relatively uniform temperature in this reaction wave results in an average reaction temperature that is very close to the maximum reaction

temperature in the unit. Because the maximum temperatures in the FTO unit are typically below 1,100°C (2,000°F), thermal  $\text{NO}_x$  is generated at very low levels relative to a conventional flame-fired fume incinerator in which maximum flame temperatures reach 1,650 to 1,925°C (3,000 to 3,500°F) (Binder and Martin 1993). Guarantees by Thermatrix of 2 ppmv of  $\text{NO}_x$  are standard when no organically-bound nitrogen is present in the fumes being treated (DeCicco 1996).

**Figure 2.6**  
Thermatrix FTO ("Top Down" Preheat)



Reproduced courtesy of Thermatrix, Inc.

### 2.3.2 Potential Applications

Soil and groundwater contamination from spills, inadequately designed landfills and surface impoundments, poorly-operated waste management facilities, and leaking underground storage tanks have occurred throughout the United States. Two common technologies for remediating these contaminated sites are air stripping for groundwater cleanup and soil vapor extraction (SVE). Each of these technologies generates an offgas that generally needs some kind of treatment before it can be discharged to the atmosphere. The FTO technology has the potential to be used as an offgas treatment process for both of these technologies.

### 2.3.3 Treatment Trains

Groundwater stripping (GWS) is a very common cleanup technology used to separate volatile organics from contaminated groundwater at remediation sites. In this process, the contaminated groundwater is pumped to a packed bed and contacted with air, which is blown through the packing. In most systems, the groundwater flow is downward through the packing. The air flow can be either up through the packing in a countercurrent mode, or cross-flow through the packing in a horizontal cross-flow scrubber (Wood et al. 1990). As the groundwater cascades through the packing, it is sheared into fine droplets by the packing and the air. Volatile organics present in these droplets of groundwater are volatilized and transferred to the air flowing through the packing, primarily by a mass transfer mechanism (Anonymous 1994).

In the SVE process, an array of vertical vents is placed in a contaminated soil. A manifold connects the vents to a vacuum pump, which is used to create a negative pressure in the vents. The negative pressure draws air through the soil and volatilizes organic contaminants in the soil, transferring them to the air. The contaminated air is drawn into the vents, through the manifold, and into the vacuum pump, which discharges it either to the atmosphere or to a treatment system. The decisions on whether to treat and the type of treatment depend on the concentration and type of contaminants present in the air (Johnson et al. 1994).

The use of the FTO as an offgas treatment process in GWS and SVE systems requires additional equipment for both pretreatment and posttreatment of the offgas. A discussion of pre- and posttreatment follows.

### 2.3.3.1 Pretreatment for GWS

In GWS systems in which entrainment of liquid water droplets might occur, the offgas from the groundwater stripper should pass through a knock-out pot followed by a flame arrestor and a mist eliminator. This offgas pretreatment minimizes impingement of droplets of entrained and condensed liquid water on to the hot packing in the reaction zone. The flame arrestor is a safeguard against flashback to potentially explosive mixtures in the knock-out pot head space. A full-scale FTO, which is treating 170 standard m<sup>3</sup>/hr (100 scfm) of an offgas from a chemical company wastewater stripper, uses this pretreatment system (Binder, Martin, and Smythe 1994).

### 2.3.3.2 Pretreatment for SVE

In SVE systems, the offgas should also pass through a knock-out pot followed by a flame arrestor. The flame arrestor is a safeguard against flashback to potentially explosive mixtures in the knock-out pot head space. This offgas pretreatment minimizes impingement of droplets of liquid water and organic condensate on the hot packing in the reaction zone. A pilot-scale FTO, which has treated 8.5 standard m<sup>3</sup>/hr (5 scfm) of offgas from an SVE system at the Department of Energy's (DOE) Savannah River Laboratory site, used this pretreatment system (Wilbourn, Allen, and Baldwin 1995).

### 2.3.3.3 Posttreatment for GWS and SVE

If the organic contaminants in the offgas that is being treated by an FTO are composed of only carbon, hydrogen, and oxygen, then it is likely that the exhaust gas can be released directly to the atmosphere without any posttreatment. If, however, the organic contaminants contain other elements, such as halogens or sulfur, then a posttreatment system, such as a packed bed alkaline wet scrubber, might be required for removing acid gases, such as HCl, other hydrogen halides, or SO<sub>2</sub>. The need for a posttreatment wet scrubber depends on the concentration of the acid gases in the FTO offgas, and US EPA and/or state regulatory performance or emission standards that are part of the specific remediation agreements for the site. Additional treatment or permitting might be required for the scrubber wastewater, which may contain chloride and/or sulfite and sulfate salts. The degree and type of scrubber wastewater permitting and/or treatment depends on site-specific

considerations and US EPA and/or state regulatory effluent and treatment standards that are part of the specific remediation agreements for the site.

A full-scale FTO, which is treating 170 standard m<sup>3</sup>/hr (100 scfm) of an offgas containing ethyl and butyl chlorides from a chemical company wastewater stripper, uses a wet scrubber as a posttreatment system to remove 99% of the HCl from the exhaust gas. The scrubber wastewater is discharged to the chemical plant's wastewater treatment system (Wilbourn 1995).

## **2.4 Plasma Furnaces**

### **2.4.1 Scientific Principles**

A plasma furnace has two high temperature reaction zones. One is the general furnace atmosphere or freeboard zone of the furnace, which is at a temperature on the order of 1,760°C (3,200°F). The second is the plasma zone in which temperatures exceed 5,500°C (10,000°F) and can approach 14,000 to 17,000°C (25,000 to 30,000°F). Chemically, the furnace atmosphere can be controlled to be oxidizing, reducing, or neutral. It operates at a higher temperature than most combustion-based incinerators; however, it does not depend upon exothermic combustion reactions to maintain its operating temperature. The volume of gases in the furnace atmosphere is not dominated by burner combustion products and the associated high volumetric flow rates of reactants is also important.

The reactor's main driving potential is the plasma zone, technically referred to as a high temperature thermal plasma. It is characterized by high viscosity, extremely high heat transfer rates, and molecular species that are predominantly ionized. The plasma is electrically neutral with an equal number of positive and negatively charged ions present. It is highly electrically conductive and, once formed, stable. Large molecules are broken down into small fragments and ionized, and the plasma incorporates simple monatomic and diatomic ions (one or two atom species). Typical reaction products from the furnace are: N<sub>2</sub>, CO, HCl, HF, H<sub>2</sub>, P<sub>2</sub>O<sub>5</sub>, O<sub>2</sub>, and CO<sub>2</sub>. Depending on the conditions present in the furnace atmosphere, oxides of nitrogen can also form.

Briefly, ionized gas, reaching temperatures of 12,000°C (21,600°F), can be shaped to form a torch or an arc in a carbon electrode furnace. Waste streams can be either pyrolyzed or oxidized as they are heated by the plasma. Bulk temperature gradients in the reactor are controlled to protect refractory linings; however, operating temperatures impact fuel gas production, efficient reduction of organic waste, and production and control of vitrified slag, and metals recovered for reuse. Reactor bulk temperatures are 1,400 to 1,750°C (2,550 to 3,180°F).

### 2.4.2 Potential Applications

Plasma furnaces operated in commercial settings frequently maintain a molten pool of metal covered by a molten layer of slag (primarily non-metal) and can process, within limits, organic material introduced with the feedstock. Several commercial vendors are promoting technologies using electrical power to reach high temperature operating conditions. Their primary goal is processing waste materials in a manner that encourages recycling of the process effluents. Some of these vendors and their furnace applications are listed in Table 2.3.

The Exide corporation, the largest lead-acid battery manufacturer with secondary lead smelting facilities, designed and tested plasma furnace technology for treating contaminated soil at a former battery recycling plant. The site had a mixture of broken-rubber (battery cases) in soil that was also contaminated with lead and lead compounds. The results of field tests on smelting lead and destroying battery casings were summarized by the US EPA (1994a) and are reproduced in Table 2.4.

### 2.4.3 Treatment Trains

A simplified equipment train for a typical plasma furnace is illustrated in Figure 2.7. The basic process steps used in plasma technologies are:

- preprocessing and introduction of waste materials into the reactor;
- preparing the neutralizing chemicals, or other additives;
- chemical reaction in the plasma reactor for effective destruction;
- separating, post-process handling, and monitoring of a low Btu synthesis gas or furnace offgas if operated in an oxidizing mode;

**Table 2.3**  
Electrically Powered Furnaces Containing Molten Slag or Metal

Company	Power Delivery	Waste Application	Reference
ABB	Resistance (Ceramic Domes)	Incinerator Fly Ash	Plumley and Boley 1990
Chem Nuclear	Resistance	Mixed Radioactive Waste	
Elkem Technologies	Carbon Electrode	Electric Arc Furnace Dust	Aune 1992; National Research Council 1993
Electro-Pyrolysis	Hollow Carbon Electrode	PCB Capacitors	Lee 1989; Titus 1992; National Research Council 1993
Exide	Hollow Carbon Electrode	Contaminated Soil	US Army 1996
M4 Environmental	Induction	Mixed Radioactive Waste	Nagel 1994
M4 Environmental	Induction	Chemical Warfare Agents	Chanenchuk 1994
Molten Metal Technology	Induction	Industrial Waste	Mather 1995; National Research Council 1993
PEAT	Plasma Torch	Medical Waste	US Army 1996
PERC	Plasma Torch	Munitions And Agents	Persoon 1996
Retech	Plasma Torch	Contaminated Soil	Geimer 1991
Retech	Plasma Torch	Chemical Warfare Agents	Eshenbach 1991; National Research Council 1993
SAIC	Plasma Torch	Mixed Radioactive Waste	Geimer 1993
Startech	Plasma Torch	Chemical Warfare Agents	Hendricks 1996
Tetronics	Plasma Torch	Spent Automobile Catalyst	Anniston, AL
Tetronics	Plasma Torch	Electric Arc Furnace Dust	Florida Steel
U.S. Bureau of Mines	Carbon Electrode	Incinerator Ash	US Army 1996
Westinghouse	Plasma Torch	Hazardous Waste	Freeman 1985; National Research Council 1993
Westinghouse	Carbon Electrode	Incinerator Ash	American Society of Mechanical Engineers and US Bureau of Mines 1994

**Table 2.4**  
**US EPA Assessments of Field Tests Smelting Lead and Destroying Battery Cases**

Source of Material	Type Of Material Tested	% Lead	Economical*	Test Results
Tonolli Superfund Site (PA)	Battery cases	3-7	yes	Lead was produced that could be reclaimed in a secondary lead smelter. Incorporate into regular blast furnace feedstock.
Hebalka Superfund Site (PA)	Battery cases	10	yes	Lead was produced that could be reclaimed in a secondary lead smelter. Incorporate into regular blast furnace feedstock.
Pedricktown Superfund Site (NJ)	Battery cases, lead containing dross, residue and debris	45	yes	Lead was produced that could be reclaimed in a secondary lead smelter. Incorporate into regular blast furnace feedstock.
Laurel House Women's Shelter (PA)	Demolition material contaminated with lead-based paint	1	no	Lead was produced that could be reclaimed in a secondary lead smelter; however, the cost of processing the material was estimated to be very high.
PennDOT	Abrasive bridge blasting material	3-5	yes	Lead was produced that could be reclaimed in a secondary lead smelter. Incorporate into regular blast furnace feedstock.

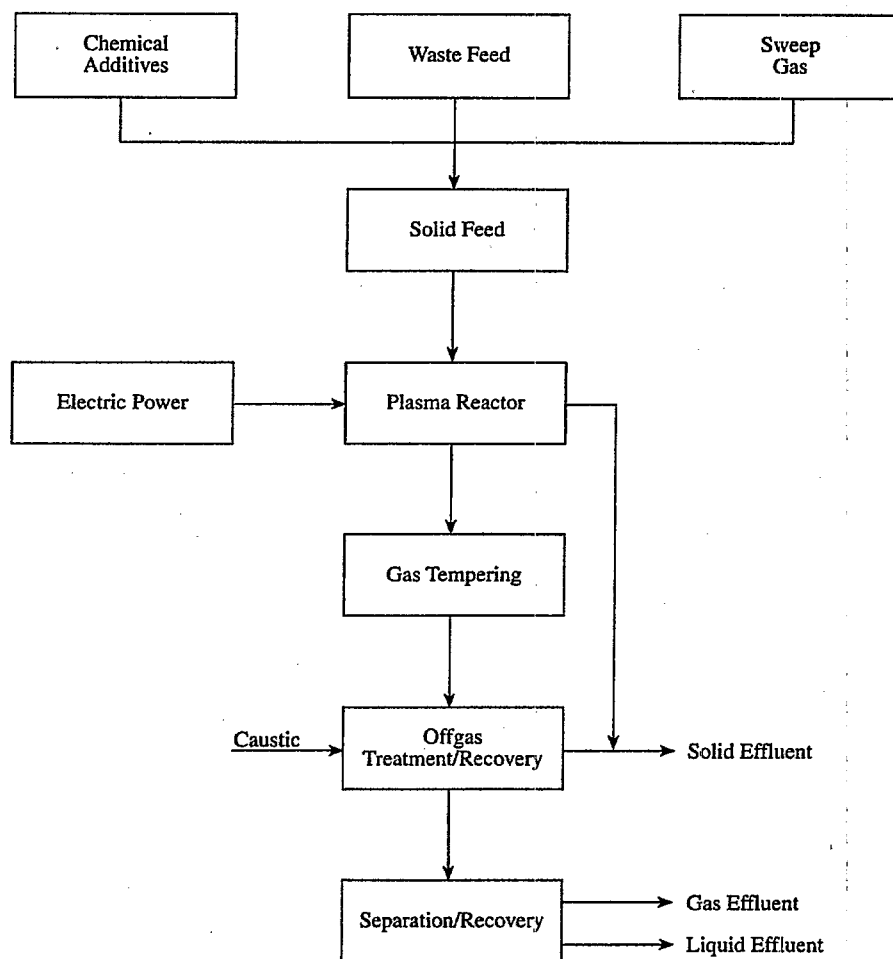
\*Economical compared with stabilization or landfill

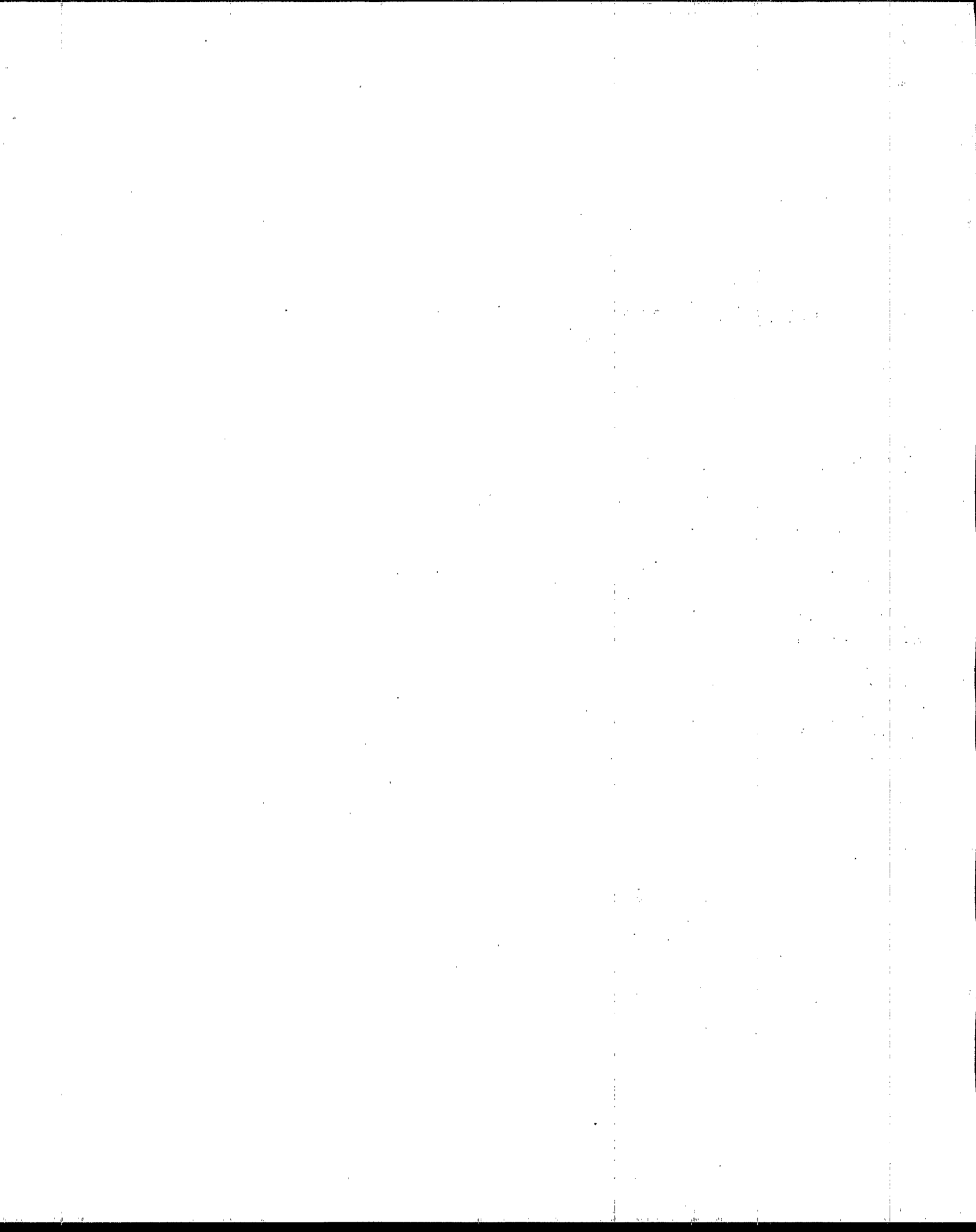
Source: US EPA 1994a



- tapping molten slag and molten metal;
- reducing offgas temperature; and
- separating and post-process handling and monitoring of solid and liquid effluents.

**Figure 2.7**  
Plasma Furnace and Auxiliary Equipment Train







## DESIGN DEVELOPMENT

### **3.1 Wet Air Oxidation**

#### **3.1.1 Remediation Goals**

A large number of waste materials and streams have been tested for possible treatment using wet air oxidation (WAO). Table 3.1 lists the range of materials that have been tested in the laboratory. Table 3.2 provides the chemical structures of some pesticides that can be destroyed by WAO; the table also includes "sulfides" as another class of compound that can be destroyed. Destruction of the toxic materials at levels of 99+% is almost always possible. Therefore, the severity of the oxidation conditions — temperature, pressure to maintain liquid phase, and residence time in the reactor — is determined by the prescribed amount of COD allowable in the process effluent. Any new feed should be tested in a batch reactor to provide design data (conversion levels and COD remaining vs. temperature and time). The usual batch reactor is a shaking bomb in an autoclave. In addition, if it is suspected that corrosion will be particularly severe, test coupons of possible materials of construction should be tested at design conditions.

The acceptability of the process to regulators and to the public depends on the toxicity of the material to be oxidized and the proximity of the plant to residential areas. It should be noted that many industrial processes operate at pressures exceeding WAO conditions. The corrosive nature of some systems under WAO conditions, however, requires special attention and proof of reliability.

**Table 3.1**  
Database of Wastes That Have Been Treated by WAO

Spent Caustics	Ethylene Scrubbing Liquors Refinery Coke Oven Scrubbing Liquors
Sludges	Municipal Wastewater Treatment Industrial Wastewater Treatment Tanning Industry Cattle, Hog, Chicken Manures
Chemical Production Wastewaters	Acrylonitrile Caprolactam Synthetic Rubber Pesticides Pharmaceuticals Food Processing Styrene/Butadiene Phenol/Acetone Refinery (Oily) Residuals Photographic Plastics/Polymers Textile/Dye
Pulp & Paper	Spent Pulping Liquors Paper Filler Recovery Sludge Conditioning Deinking Sludges
Commercial Waste Treatment	Phenolics Cyanides Sulfidic Pesticides Solvent and Solvent Still Bottoms General Organics Drum Washings
Military Wastes	Propellants Red Water
Miscellaneous Applications	Metallurgical Extractions Powder Carbon Regeneration Coal Oxidation and Desulfurization Vanillin Production Peat Dewatering Oxygen Pulping

Source: Copa and Lehmann 1992

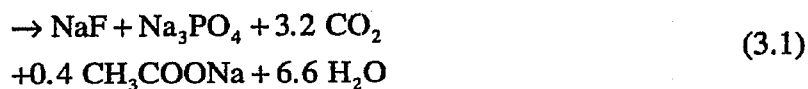
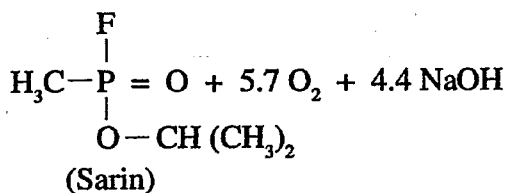
**Table 3.2**  
Technical Basis for Data Extrapolation

Wet Air Oxidation: Chemical Structures Destroyed

Glyphosate (Roundup)	Phosphono $\begin{array}{c} \text{O} \\   \\ -\text{P} < \begin{array}{l} \text{O}- \\ \text{O}- \end{array} \end{array}$
Diazinon Dursban Parathion	Phosphorothio- $\begin{array}{c} \text{S} \\   \\ -\text{O}-\text{P} < \begin{array}{l} \text{O}- \\ \text{O}- \end{array} \end{array}$
Betasan Dimethoate Disufoton Dyfonate Imidan Malathion Phorate	Phosphorodithio- $\begin{array}{c} \text{S} \\   \\ -\text{S}-\text{P} < \begin{array}{l} \text{O}- \\ \text{O}- \end{array} \end{array}$
Spent Caustic	Sulfides (Organic and Inorganic) Mercaptans

### 3.1.2 Design Basis

A sample mass balance is presented below to illustrate flow rates, products expected, reactor dimensions, etc. Sarin is a nerve agent with a structure resembling some of the pesticides chosen for study. The WAO of this material, with NaOH added to the mixture for pH control, approximately follows Equation 3.1; note that substantial residual organic material remains in the product solution; this is shown in Equation 3.1 as sodium acetate, but other low molecular weight oxygenated species will also be present.



Equation 3.1 does not show nitrogen supplied with the air, nor does it show low levels of other materials present in the gas phase. The products withdrawn from WAO of Sarin, based on data with pesticides, are anticipated to have the characteristics shown in Table 3.3.

**Table 3.3**  
Sarin Wet Air Oxidation Products

Products	Concentration Range
<b>Offgas</b>	
Oxygen	3-6% (by volume)
Nitrogen (mainly from air)	78-82% (by volume)
Carbon Dioxide	8-12% (by volume)
Carbon Monoxide	10-1,000 ppm
Organics	100-1,000 ppm
<b>Liquid</b>	
Biochemical Oxygen Demand (BOD)	5,000-10,000 mg/L
Chemical Oxygen Demand (COD)	10,000-20,000 mg/L
<b>Solids</b>	
Salts, such as NaF, $\text{Na}_3\text{PO}_4$ , excess NaOH, etc. Other materials could lead to other salts, such as NaCl, depending on feed composition.	

Source: Copa and Lehmann 1992

Both the offgas and the liquid require further treatment. The gas is subjected to either thermal or catalytic oxidation. The liquid is diverted to a biological wastewater treatment plant for complete detoxification of the remaining organics. Solids are recovered from the liquid by vaporization and sent to a landfill.

Corrosion can be a problem under WAO conditions, particularly for materials containing species such as chlorine, fluorine, and sulfur, which yield strong acids upon oxidation. Control of pH will be required in such cases; in

the example of Equation 3.1, sodium hydroxide was added. The addition of a caustic might also influence the amount of solid product. The pH is normally maintained below 8 to prevent the caustic from reacting with  $\text{CO}_2$  to form carbonate. Materials with a large content of chlorine, fluorine, etc., might require a pH up to 11 for corrosion control. Most of the carbon dioxide will be reacted to carbonate as a result, with a consequent large increase in the process solid residue. This has not been shown in Equation 3.1; a rough estimate for it has been included in the following material balance.

An approximate material balance has been calculated with estimates for the size of equipment and the product streams (National Research Council 1993). The oxidizing gas in this case was oxygen-enriched air.

The mass balances are based on the following:

- feed: 1,000 kg of Sarin;
- oxygen: 25% excess over theoretical;
- enriched air:  $\text{O}_2/\text{N}_2 = 1/1$ ;
- NaOH added to produce a 3 molar solution after reaction (this is a large excess of NaOH and is included for corrosion control; testing would be needed to better judge what is required);
- 20% of C-H in the feed is left as sodium acetate; and
- the  $\text{CO}_2$  content of the gas is an estimate and is not based on equilibrium with liquid.

**Feed (Input):**

- Sarin: 1,000 kg (7.14 kg mol)
- Water: 19,000 kg (1,056 kg mol)
- NaOH: 4,770 kg (119 kg mol)
- $\text{O}_2$ : 50.7 kg mol
- $\text{N}_2$ : 50.7 kg mol

**Gas Phase (Output):**

- $\text{O}_2$ : 16.0% by volume (dry basis)
- $\text{N}_2$ : 81.7% by volume

- CO<sub>2</sub>: 2.3% by volume
- CO: 500 ppm
- Hydrocarbons: 500 ppm
- Volume (dry basis): 62.1 kg mol =  $1.52 \cdot 10^3 \text{ m}^3$  @  
Pressure = 1 atm (1 bar) and Temperature = 25°C (77°F)
- H<sub>2</sub>O in gas phase at reactor conditions  $\approx 62 \text{ kg mol}$

**Liquid Phase (Output):**

- H<sub>2</sub>O: 19,118 kg
  - NaF: 300 kg
  - Na<sub>3</sub>PO<sub>4</sub>: 1,171 kg
  - Na<sub>2</sub>CO<sub>3</sub>: 2,271 kg
  - CH<sub>3</sub>COONa: 234 kg
  - NaOH: 1,799 kg
- Total 24,893 kg (54,765 lb)
- Reactor volume (assuming feed = 1,000 kg of Sarin/day (0.5 volume of feed per hour per volume of reactor) 2.6 m<sup>3</sup> (92 ft<sup>3</sup>))
  - Length = 7 m (23 ft); Diameter = 0.68 m (2.2 ft)

The calculations demonstrate that the volumes of material to be handled and the inorganic residue are many times greater than the volume of original toxic material to be destroyed. They also demonstrate that it would be quite practical to operate WAO as a closed system with material released from the process only after analysis. For example, based on processing 1,000 kg Sarin/day, the resulting volume of by-products would be:

- liquid holdup for 8 hours retention time = 8,300 kg (18,260 lb)(approximately 8 m<sup>3</sup> [280 ft<sup>3</sup>]); and
- gas holdup for 8 hours' retention, at 25°C (77°F) and 60 atm (60 bars) = 8.4 m<sup>3</sup> (300 ft<sup>3</sup>) on a dry basis.

The volumes of both liquid and gas for 8-hour retention time are modest.

The compositions shown above change under upset conditions. A low inlet temperature will quench the reaction, leading to little oxygen consumption and little organic destruction, whereas a high inlet temperature will yield



more complete oxidation to  $\text{CO}_2$  and  $\text{H}_2\text{O}$  and possibly an undesirable temperature excursion. Both conditions will lead to a shutdown. In the first case, the unreacted material is recycled to a feed tank.

### 3.1.3 Design and Equipment Selection

Design and equipment selection will depend on the nature of the feed: its concentration in water, its chemical composition, and toxic hazard.

If the feed is highly diluted, e.g., less than 1%, heat exchange must be provided to increase the temperature close to final design temperature. If the feed is relatively concentrated, e.g., more than 5% in water, heat exchange (cooling) will probably have to be provided to control the final temperature. A complete energy balance will be needed to finalize the design.

The extent of oxidation required will vary with the feed and nature of the product. For example, sewage to be treated to improve its de-watering will be treated at low temperature (and relatively low pressure); a chemical pesticide which needs complete destruction will require higher temperature and longer residence time. Specific details can best be determined on the basis of previous experience, or by tests in a pilot plant (shaking autoclave).

A feed with a composition that will yield a strongly acidic product will require special treatment, e.g., a chlorine-containing material such as PCB which will produce hydrochloric acid. Corrosion control in this case will probably require addition of a caustic to the feed to control pH. The extent of corrosion problems may also be determined by preliminary pilot plant tests.

### 3.1.4 Process Modifications

Corrosion has been emphasized as a serious problem. Stainless steel (304L, 316L) has provided adequate resistance to corrosion for most commercial applications; 316L is now preferred. Materials with high concentration of chlorine and fluorine, etc., pose more severe corrosion problems because of their strong acid formation. Other potential materials of construction are Incoloy 800, 825; Inconel 600, 625; Hastelloy C-276, G-3, C-22; Carpenter 20 CB-3; or various grades of titanium. Corrosion test work on possible materials with simulated product solutions, under WAO temperature and pressure conditions, should be done before any plant construction. Corrosion test work applicable to supercritical water oxidation of

some materials has been carried out, but it is not clear that this test work is directly applicable to WAO conditions.

Commercial WAO units have operated on very dilute feeds (less than 2%), because of their advantage over other technologies for low concentrations. At higher concentrations, there could be large temperature excursions, raising the possibility of unstable operation.

The system has some built-in safeguards. Increased heat release causes only modest temperature rise because (1) the large heat capacity of the water present moderates temperature increases; and (2) increased vaporization of water automatically occurs. Finally, temperature can be controlled by modulating the air flow. There is no gas-cap maintained in the reactor, and oxygen solubility is limited. Cutting off the air flow shuts down the reaction quickly.

Testing is usually done in batch reactors, whereas commercial units are operated continuously. Some design features help in adapting the test data to flow conditions:

- The flow systems are usually baffled, so that the reactors do not behave as completely stirred tank reactors (CSTRs); instead, they are constructed with some of the characteristics of plug flow reactors and resemble batch reactors in their kinetics. In some cases, two or more reactors have been run in series, again approximating plug flow kinetics.
- Occurrence of an induction period could be a special complication, with a major effect on a batch reactor. The commercial designs have their first baffle approximately halfway up; thus, the bottom half of the reactor comes close to CSTR operation and provides a continuous source of the reactive intermediates required to end any induction period.

Batch laboratory data are useful, but testing under continuous flow (plant) conditions is always desirable for a new application. Portable, sled-mounted units have been used for this purpose (National Research Council 1993).

### 3.1.5 Pretreatment Processes

The process can handle a wide variety of feed materials with no pretreatment required. However, the concentration of pollutant(s) and the physical characteristics of the water, may require some pretreatment.

Water may be added to feedstocks that are too concentrated. For feedstocks which are too dilute, extra heat must be provided; this has sometimes been done by adding some extra material (fuel) to the aqueous feed, to provide added heat of combustion in the reactor.

A feedstock that will produce a strongly acidic solution may call for pretreatment with caustic to control pH in the reactor.

Insoluble feedstocks can be handled by breaking up and dispersing in water. Alternatively, a pretreatment to solubilize the material may be helpful, e.g., hydrolysis of a nitrocellulose propellant.

### 3.1.6 Posttreatment Processes

The example cited in Section 3.1.2 produced a liquid effluent with a COD of 10,000 to 20,000 mg/L. This would need to be reduced, probably by a biological wastewater treatment plant, before discharge to the environment. The usual products — such as low molecular weight carboxylic acids — respond well to biological posttreatment.

The carbon monoxide and hydrocarbons in the effluent gas may be excessive require oxidation before release.

### 3.1.7 Process Instrumentation and Controls

Reactor flow and pressure control are standard. Temperature control is critical; too low a final reactor temperature will affect the conversion level and too high a temperature could drive up the pressure and force a shut-down. Most instrument response times are not very demanding, as suggested by the typical feed residence times in the reactor of one-half hour or more.

The gas residence time is much shorter; it is measured in seconds. Therefore, offgas is monitored continuously with on-line analyzers. Parameters to be monitored are: oxygen, nitrogen, carbon dioxide, carbon monoxide, and at least one product characteristic of the oxidation products, e.g., an intermediate in the oxidation process. The product gas may require treatment before

release (e.g., catalytic oxidation), and would require monitoring both before treatment and upon release.

### 3.1.8 Safety Requirements

The operating temperature and pressure of a WAO unit may be high, e.g., up to 316°C (600°F) and 11.7 MPa (1,700 psi), though lower for most units. These are not unusual conditions, and are well within state-of-the-art-technology. All equipment must be built to meet appropriate code requirements.

Typical of industrial equipment, hazards result from off-specification operation — in this case, too high a temperature and pressure. The time-constant for transient temperature change is long, certainly many minutes, due to the relatively large volume of water in the reactor and the small concentration of feed material. In addition, any temperature increase is limited by the pressure; the water will boil when it reaches its boiling point.

The response to a temperature rise above the preset operating window is to shut off the feed. Any further temperature rise is then limited by the small concentration of oxidizable feed remaining in the water.

### 3.1.9 Specification Development

Process and equipment specification and materials of construction are determined by the nature of the feed and the product requirements. Key operating variables and process results requiring specification are:

- anticipated range of feedstock composition, concentration in water in particular;
- reactor operating conditions: temperature, residence time, pressure, and air flow rate;
- liquid effluent composition, particularly the level of destruction of the feed material required; and
- offgas composition, particularly the level of some prescribed product of the oxidation process.

In cases where the feedstock is a new material that has not been tested or processed previously, some preliminary (pilot-plant) experimental work will probably be required to set operating specifications.

### 3.1.10 Cost Data

A range of capital costs, as well as operation and maintenance costs, has been presented by U.S. Filter-Zimpro (Copa and Lehmann 1992) and depicted in Figures 3.1 and 3.2. These do not reflect any costs for environmental impact assessments, permitting, testing/research/development required before design, special materials of construction required for particularly severe corrosion problems, the cost of additional chemicals required, or any costs for posttreatment.

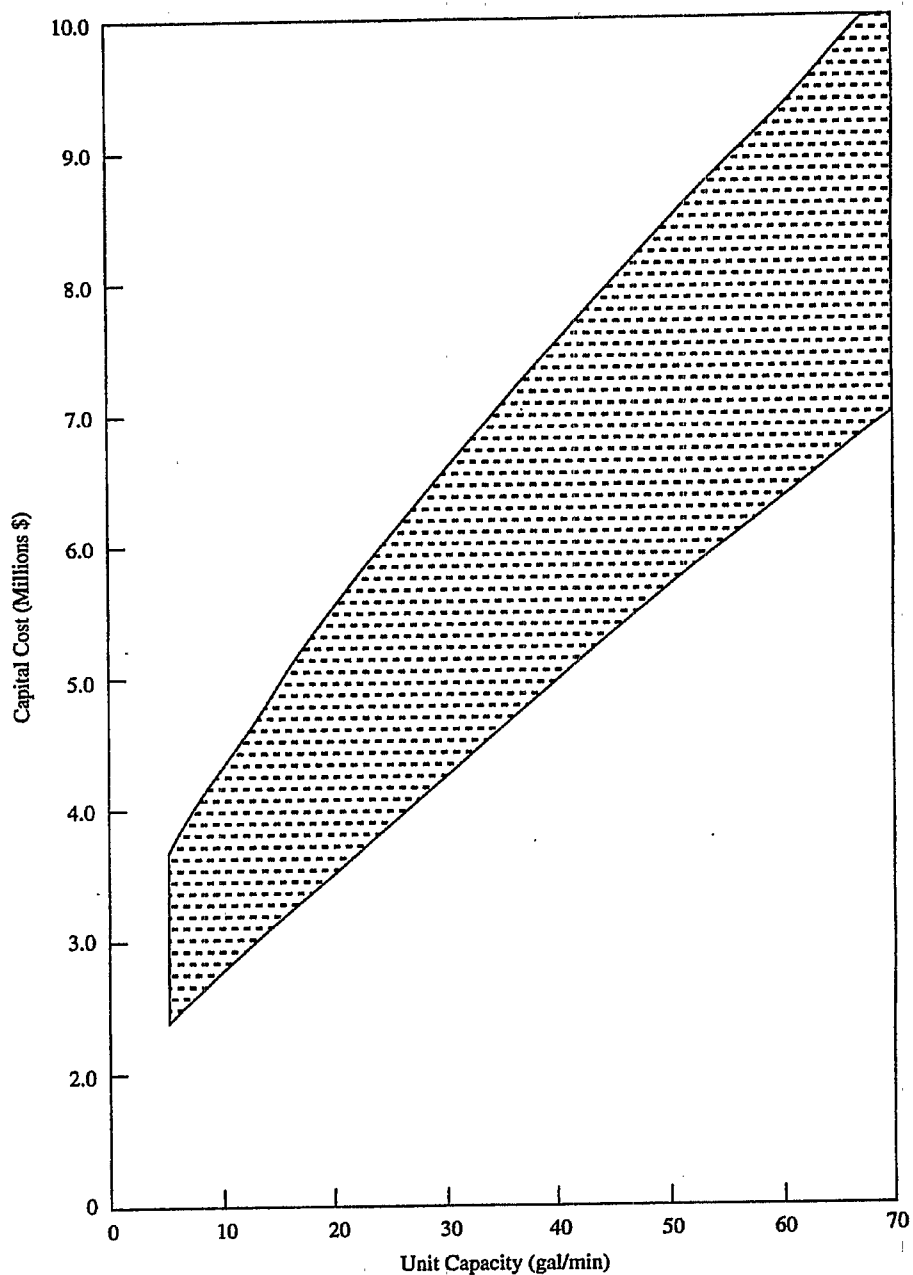
The capital cost (Figure 3.1) increases with the flow rate of total liquid. The total overhead and maintenance (O & M) cost also increases with the flow rate. It is clear that costs increase with dilution. As mentioned, most applications of WAO have been to toxic materials which are already highly diluted. Where some additional dilution is required, it is desirable to minimize its extent, consistent with a stable process operation.

The costs depicted Figures 3.1 and 3.2 have been applied to develop the following crude cost estimates for a plant capable of destroying 1.8 tonne/day (2 ton/day) of the nerve agent Sarin (Equation 3.1). It was assumed for these estimates that the plant life was 5 years, its availability was 90%, the cost of money was 10%, and there was zero salvage value.

O & M cost	\$675/ton/day
Capital Cost (\$6M)	\$3,170/ton/day
Total	\$2,845/ton/day

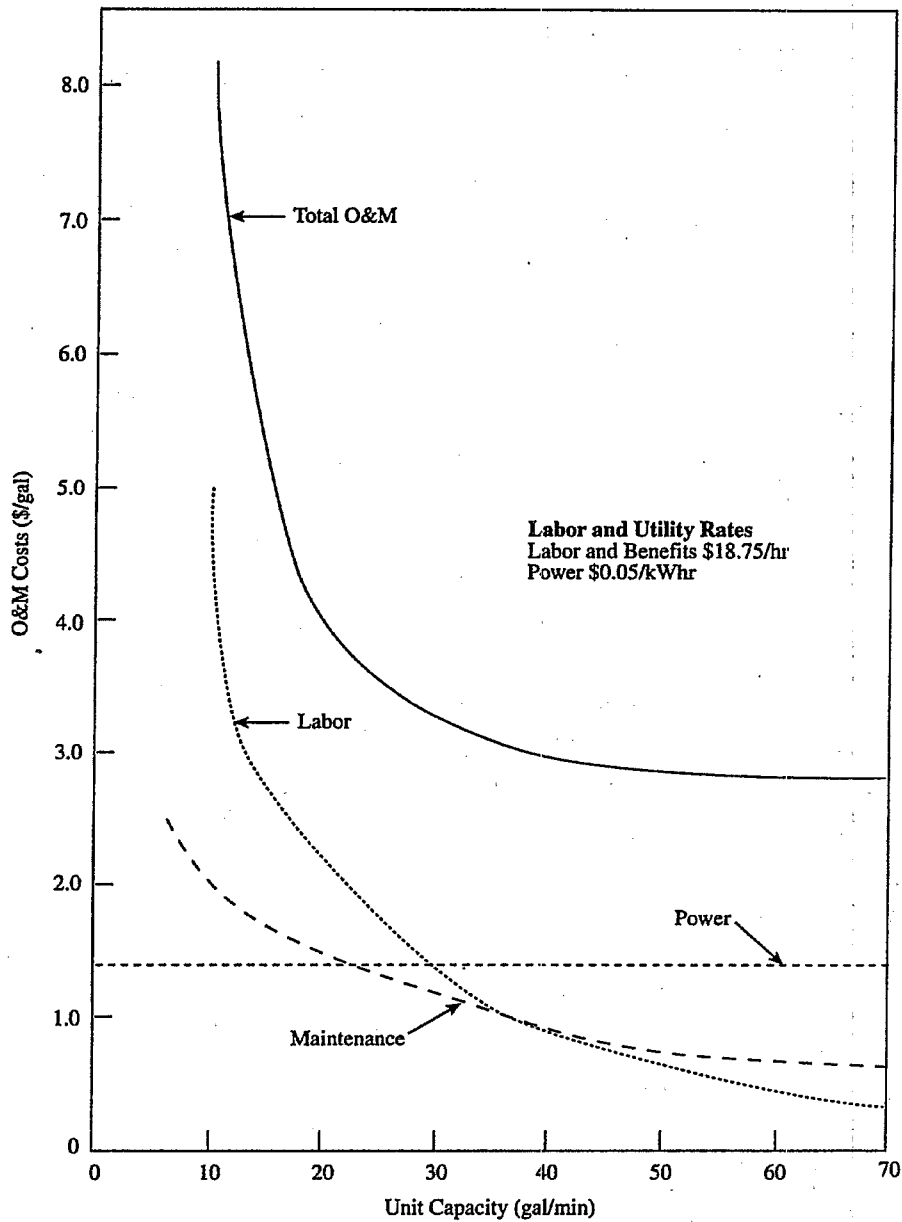
This cost translates to \$3.13/kg of Sarin destroyed, or about \$500/barrel. Realistically, costs for destruction of Sarin will be much higher (many-fold higher). The costs for destroying toxic materials are frequently driven by factors other than the engineering and direct operating costs given in the example above. These include costs for design reviews required by regulatory agencies, tests on surrogates to demonstrate performance, start-up delays due to public concern for safety, quantitative risk assessments and health risk assessments that may be required before startup, etc. These additional costs depend on the site (proximity to population centers), and on the toxic material being destroyed. For reference, the cost of destroying the very toxic agent Sarin by incineration has proven to be many-fold larger than the 'normal' direct engineering and operating costs; the same will probably be true for other disposal processes.

**Figure 3.1**  
Hazardous Waste Wet Oxidation  
Installed Capital Costs vs. Wet Oxidation Unit Capacity



Source: Copa and Lehmann 1992

**Figure 3.2**  
Operating and Maintenance Costs for WAO Units



Source: Copa and Lehmann 1992

### 3.1.11 Design Validation

The engineering design will probably experience more than one review before construction as part of design development and permitting. These reviews should ensure that local conditions and limitations have been properly considered.

The design package will usually contain some guarantee of performance. Therefore, validation of the design will be based on a performance test carried out under conditions defined in the performance guarantee.

### 3.1.12 Permitting Requirements

The permitting process will depend on the nature of the waste. The state regulatory agency should be notified as early as possible of the problem to be addressed, and the general plan. In turn, they will define their requirements for information to be submitted and the emission standards to be satisfied.

It is helpful if the regulatory personnel have had experience with WAO. If not, the process will have to be explained and performance data from other WAO units will need to be presented. Ultimately, very complete process-flow diagrams, with piping and instrumentation, will probably be required.

Wet Air Oxidation is not a new, untried technology. In view of its history, it should be possible to obtain construction and operating permits. It must be recognized, however, that permitting requirements are usually site-specific.

### 3.1.13 Performance Measures

Offgas from WAO is monitored by on-line analyzers for oxygen, nitrogen, carbon dioxide, carbon monoxide, and total hydrocarbon. Ammonia can also be determined by gas scrubbing and liquid analysis, if necessary. The gas product of the WAO unit should be monitored as part of the operating control, e.g., analysis for excess oxygen. In addition, the gaseous effluent from any posttreatment unit, such as catalytic oxidation, will need analysis. Gas released to the atmosphere will need to be tested for residual feed material, with provision for immediate plant shut-down if any is detected.

The wastewater is usually analyzed for conventional wastewater parameters: COD, BOD, solids, ash, pH, total Kjeldahl nitrogen,  $\text{NH}_3$ , etc. Gas



chromatography, liquid chromatography, and gas chromatography/mass spectroscopy (GC/MS) have been used for specific organic constituents and are the methods of choice for analyzing the effluent liquid for residual toxic feed material. The solid salts produced should be classified as nonhazardous, but will require detailed analysis before disposal. Solid products from any biological posttreatment of the liquid must be tested for toxicity before disposal.

The oxidation process is exothermic, with large activation energies in some cases. The process must be controlled to avoid unstable operation with large temperature excursions. A high level of dilution (1% solution) will limit this type of problem. At higher concentrations (5%), it is necessary to set an operating window, with plant shut-down triggered by any departure from the design limit.

### 3.1.14 Design Checklist

The key information to be compiled and/or developed during design includes:

- plot plan, with any limitation set by adjoining constraints;
- utility supply — by the owner, by outside supplier;
- process requirements set by the owner, for example permit requirements;
- possible interference with adjoining operations during tie-in to utilities etc.;
- public sensitivities, e.g., proximity to housing, schools, etc., and impact on such things as acceptable noise-level (e.g., compressor noise) etc.;
- materials of construction of various parts of the plant, and test work required to show that materials specifications have been met;
- major component checklist;
- piping and instrumentation diagrams; and
- control room layout.

## **3.2 Texaco Gasification Process**

### **3.2.1 Remediation Goals**

The Texaco Gasification Process (TGP) is widely used for producing hydrogen and synthesis gas in the refining and petrochemical industries from low heat value feedstocks, such as petroleum residuals and coal. These raw materials sometimes contain significant concentrations of metals plus sulfur, chlorine, and nitrogen compounds. The industry has developed processes to remove such impurities which are available for licensing for specific applications and are also applicable to waste treatment. Generally, these processes can remove impurities from the product gas stream to levels below those required by current US EPA regulations.

The gas treating system produces fused slag, inorganic fines, and a waste gas stream consisting mainly of  $\text{CO}_2$  and  $\text{N}_2$ , as well as smaller amounts of methane, volatile metals, and any residual sulfur, chlorine, and nitrogen compounds that escape the gas treating system. The low volumes of process waste gas and wastewater allow these waste streams to be economically stored and analyzed prior to release. This way, plant personnel can verify that the waste streams meet regulatory requirements.

The high temperature and elevated pressure and the use of coal with an accompanying increase in solid waste could generate some concern by regulators and the public. These concerns tend to be very site-specific and less concern is expected near existing industrial sites where comparable operations are underway. Greater concerns might be encountered at sites surrounded by residential communities.

### **3.2.2 Design Basis**

The TGP support considerations include site conditions (surface, subsurface, clearance, area, topography, climate, and geography), utilities, facilities, and equipment.

For a 90 tonne/day (100 ton/day) transportable waste processing unit, surface requirements include a level, graded area capable of supporting the

equipment and the structures housing it. The complexity and mechanical structure of a high-temperature, high-pressure TGP unit mandate a level and stable location. The unit cannot be deployed in areas where fragile geologic formations could be disturbed by heavy loads or vibrational stress. Foundations must support the weight of the gasifier system, which is estimated at 45 tonne (50 ton), as well as other TGP support facilities and equipment. The transportable TGP unit weighs approximately 270 tonne (300 ton) and consists of multiple, skid-mounted trailers requiring stable access roads that can accommodate oversized and heavy equipment.

The transportable 90 tonne/day (100 ton/day) TGP unit requires an area of approximately 3,700 m<sup>2</sup> (40,000 ft<sup>2</sup>), 83 m by 46 m (275 ft by 150 ft), with height clearances of up to 21 m (70 ft). This area should accommodate all TGP process operations, although additional space could be needed for special feed preparation and waste residuals storage facilities.

The transportable TGP unit can be used in a broad range of different climates. Although prolonged periods of freezing temperatures might interfere with soil excavation and handling, coal handling, slurry preparation, and water-related operations, they would not affect a TGP design that incorporates adequate heating, insulating, and heat-tracing capabilities at critical locations.

The transportable 90 tonne/day (100 ton/day) TGP unit requires the following supplies: 83 tonne/day (91 ton/day) of oxygen, 35 tonne/day (39 ton/day) of coal, 4.5 tonne/day (5 ton/day) of lime, 431 MJ/hr (410 kW/hr) of electrical power, 2.5 L/sec (40 gal/min) of makeup water, and less than 900 kg/day (1 ton/day) of nitrogen.

The support facilities required include staging areas for contaminated soil and coal prior to pretreatment, materials-handling, and slurry preparation. Syngas product can be routed by pipeline directly off-site without any support facilities for storage or transport. Solid products would be stored in roll-off bins. Wastewater would be collected in an appropriate size storage tank. All support facilities must be designed to control runoff and fugitive emissions. Support equipment required includes excavation/transport equipment, such as backhoes, front-end loaders, dump trucks, roll-off bins, and storage tanks.

### 3.2.3 Design and Equipment Selection

The major information needs for applying this technology at a specific site are:

- range of composition and properties of the wastes to be treated;
- amount and rate of delivery of the waste material to the gasification system;
- tests in pilot facilities of representative samples of the wastes to be treated. These would include tests in the existing gasification pilot facilities to establish optimal conditions and also to provide samples for studies leading to specification of posttreatment processes;
- regulatory requirements and costs of disposing of the process waste streams; and
- site area available for the process. An area of approximately 3,700 m<sup>2</sup> (40,000 ft<sup>2</sup>) plus land for storage of feed material and waste streams is needed.

### 3.2.4 Process Modifications

It is anticipated that the feed system and the gas cleanup system will be matched to the specific wastes to be treated and to meet the environmental requirements for disposal of the gas, liquid, and solid waste streams produced.

### 3.2.5 Pretreatment Processes

The TGP requires a steady supply of the material to be treated in a physical form that is suitable for the process. While liquid and gaseous feeds can be injected directly into the reactor, solids are mixed with water to form a pumpable slurry that is sufficiently stable to allow averaging of composition and physical properties by storage in the feed system.

The particle size must be small enough to form a pumpable slurry. Coarser materials require grinding and/or sieving to meet the size requirement. Additives can be used to adjust slurry properties or control slag characteristics, such as viscosity. If the waste exhibits unusual physical or chemical characteristics that would affect the ability of the pretreatment

module to slurry the feed, additional pretreatment equipment can supplement the existing design (US EPA 1995). A typical feed slurry contains 60 to 70% solids by weight. Recycled fine solids from the slag separator and the gas cleanup system can also be added to the feed system.

### 3.2.6 Posttreatment Processes

#### 3.2.6.1 Solids Residuals

Solid TGP by-products, such as course slag, fine slag, and clarifier solids, are stored and characterized to allow proper disposal based upon their hazardous or nonhazardous characteristics (US EPA 1995).

Most of the inorganic compounds of the waste form a molten slag which, on cooling, is expected to have sufficiently low solubility to pass US EPA leaching tests. If solubility is a problem, additives might be required in the feed to reduce the solubility. This material can then be disposed in a waste landfill or it can, in some cases, be used as aggregate or for paving.

Some inorganic fines leave with the gas produced and are captured by filtration in the gas treatment system. If these particles do not contain volatile components, the fines can be recycled to the gasifier and then disposed along with the rest of the slag. If volatile metals, such as lead, exist, they concentrate in the fines and then the fines must be disposed as a separate toxic waste stream.

#### 3.2.6.2 Gas Stream

The gas leaving the gasifier quench section contains fine particulates and a variety of gaseous impurities ( $\text{CO}_2$ ,  $\text{HCl}$ ,  $\text{H}_2\text{S}$ ,  $\text{NH}_3$ , etc.). The traditional petrochemical uses for synthesis gas in production of ammonia, methanol, and other products require partial removal of  $\text{CO}_2$  and nearly complete removal of hydrogen sulfide and other acid gases. The cleanup requirements for use of the gaseous product as fuel can be easily met by existing processes suitable for production of gas for use in sensitive catalytic processes (Astrita, Savage, and Bisio 1983). If very volatile components, such as mercury, are present, a separate treatment step, such as activated carbon adsorption, might be required.

### 3.2.6.3 Process Wastewater

Although the chemical reactions that drive the gasification process (Equations 2.1 and 2.2) indicate net water consumption for a dry feed, the feed slurry generally contains surplus water. This water, if combined with water from cooling and scrubbing, can produce a wastewater stream that might require treatment before disposal. For the Superfund Innovative Technology Evaluation (SITE) project discussed in Chapter 5, a wastewater stream was produced that would probably need treatment. The impurities in the water are specific to the waste and fuel compositions. Appropriate water treatment processes are available and their selection would be part of a site-specific design.

### 3.2.7 Process Instrumentation and Controls

It is anticipated that process instrumentation and controls for the reactor would be essentially the same as those used in current operating plants. For the feed preparation and injection systems, it may be necessary to adapt the instrumentation and controls to the specific feeds being treated; however, Texaco's systems for handling both solid and liquid feedstocks will not require major modification.

The gas stream monitors and controls used in commercial synthesis gas production with its stringent purity requirements should be more than adequate for waste treatment. The possible exception to the foregoing is if chlorine compounds are present.

The liquid and solid wastes produced must also meet increasingly stringent purity requirements which may call for some requirements for instrumentation and control beyond those currently used in industrial installations. It is believed that equipment and technology are available to meet these requirements.

### 3.2.8 Safety Requirements

Apart from the conventional safety requirements for the feed handling system and the gas cleaning system, the reactor operation at high temperature and moderately high pressure introduces additional considerations. Leaks of flammable gas must be dealt with by adequate dilution by surrounding air under all operating conditions. The remote possibility of catastrophic reactor failure might require special containment for heavily-populated areas.

### 3.2.9 Specification Development

It will be necessary to develop performance specifications to ensure that the wastes will be converted into satisfactory product streams at the required rates. Since the technologies and treating requirements can be expected to differ somewhat at each site, these performance specifications will require some development for each installation and would logically be part of the licensing process.

### 3.2.10 Cost Data

Estimates of the cost to treat contaminated soils and sludges with TGP were prepared by Texaco based on the performance data from the demonstration at Montebello Research Laboratory (MRL) which is discussed in Chapter 5. The demonstration was conducted in a pilot facility of a size that would be impractical for an on-site cleanup or for a commercial facility. Texaco has designed a transportable gasifier that would be suitable as a minimum size for site cleanup contracts. The small gasifier falls within the size range of commercial plants and is less than one-tenth the size of the largest operating TGP. The pilot facility at Montebello is used to optimize operating conditions for the design of commercial units.

Results from this demonstration were applied to a probable commercial configuration. Soil with approximately the same composition of that used in the SITE Demonstration was used as a basis for the commercial design and economic analysis. This soil would be slurried with 5% lime and 34.65 tonne/day (38.19 ton/day) of coal in water to produce a feedstock of 62.5% solids and fed to the unit at the rate of 90 tonne/day (100 ton/day). This feedstock with coal would have a gross heating value of 5,555 Btu/lb dry which compares to the average gross heating value of 6,133 Btu/lb during the demonstration. More oxygen would be required per pound of feed to offset this difference in heating value. Since the TGP is being used for site remediation, the soil throughput has been maximized.

The costs have been placed into twelve cost categories applicable to typical cleanup activities at Superfund and RCRA corrective action sites and are discussed in turn in the following subsections.

### 3.2.10.1 Issues and Assumptions

This analysis is based on operating the TGP with the demonstration soil with a minimum of coal and oxygen. The demonstration soil has about 20% combustibles that partly offset the amount of auxiliary fuel required to maintain the gasification reaction. Other soils might not have as much heating value.

Even with low-Btu feedstocks, the TGP converts waste to useful syngas. Any proposed cleanup activity should take into consideration practical uses for the syngas. The simplest uses for syngas are as a gaseous fuel for steam production or power generation. These uses are not included in this economic analysis. Because the capital equipment and its installation represent a high percentage of the total project cost, TGP should be considered for larger cleanup activities.

A transportable system can be designed to be used at several sites over its usable service life; fifteen years is assumed for this analysis. Because relocation can be expensive, the more practical investment might be at a central location for the entire life of the equipment — perhaps thirty years. Both alternatives are presented for comparison.

The transportable TGP system is rated at 90 tonne/day (100 ton/day) of soil and is assumed to be set up at three sites and operated for about four years at each during its fifteen-year life. The central TGP system is rated at 180 tonne/day (200 ton/day) of soil and is assumed to be operated at a fixed location for fifteen years. Both systems are assumed to operate 24 hours per day, seven days per week. Capacity utilization factors of 70% and 80% are included to allow for both scheduled and unplanned outages. The costs for the transportable unit are based on three sites with 90,000 tonne (100,000 ton) of soil each. That is a rate of 90 tonne/day (100 ton/day) at 80% utilization for 3.42 years. The cleanup of the same site at 70% utilization would require 3.91 years and would result in higher labor and maintenance costs.

### 3.2.10.2 Site Preparation Costs

The costs for excavation and on-site transportation of a contaminated soil vary widely. No estimates of the cost of waste handling nor of the temporary roads and facilities that might be required are included because they are site-specific. The costs for foundations, utilities, and equipment erection for the TGP systems can be estimated and are included in the Capital Equipment subsection, 3.2.10.4.



### 3.2.10.3 Permitting and Regulatory Requirements

The costs for permitting are not included. These include federal, state, and local permits and will vary with each project and are generally the obligation of the site owner or responsible party. Depending on the site, these costs could be significant in terms of time and money. The monitoring and analytical protocols that would be required on an ongoing basis during operation have been estimated and are included under subsection 3.2.10.10, Analytical Services.

### 3.2.10.4 Capital Equipment

The capital costs are based in part on a firm quotation in 1993 received by Texaco for a modular gasifier for soil remediation. This quotation included about two-thirds of the equipment included in this estimate. The balance of the installed equipment, including that required for feed preparation, gas cleaning, and wastewater treatment, was estimated by Texaco. The costs of the 180 tonne/day (200 ton/day) central plant were extrapolated from the costs developed for the 90 tonne/day (100 ton/day) transportable plant. For the transportable unit option, it is assumed that the same unit would operate at three sites over its fifteen-year life. The capital costs are based on amortization over fifteen years at 8% interest with no tax considerations and no salvage value. The annual capital recovery (amortization) factor is 0.11683, and the total was allocated evenly between the three sites or 58.4% of the capital cost for each. Table 3.4 lists the capital cost for the 90 tonne/day (100 ton/day) TGP unit.

The implementation costs are for the labor and contracts for site preparation, equipment installation, utility service connections, and equipment check-out. The transportable system occupies approximately one-half acre and requires 16 weeks for installation. The major contracts are for foundations and slabs, equipment and structural erection, electrical, and controls and instrumentation. The total is estimated at \$2,500,000.

Most of the components for the transportable TGP unit are shipped in factory-built, structural modules. The largest of these will be 12.8 m by 4.3 m by 4.3 m (42 ft by 14 ft by 14 ft). Transportation was estimated on the basis of relocation from Texas to California or Illinois.

The implementation costs for the central plant are one-time costs and are included with the capital equipment estimate.

**Table 3.4**  
Capital Cost for the 90 tonne/day (100 ton/day)  
Texaco Gasification Process Unit

	Capital Cost (Thousands of \$)
a Feed Receiving and Storage	\$1,000
b Grinding and Slurry Preparation	700
c Gasification	1,600
d Lockhopper	800
e Syngas Cleaning	600
f SulFerox*	1,900
g Slag and Solids Handling	400
h Wastewater Treatment	300
i Control System	700
j Utilities and Support Facilities	1,000
k Engineering	2,000
<b>Total Cost</b>	<b>\$11,000</b>

\*Proprietary hydrogen sulfide treatment module

### 3.2.10.5 Labor

Labor costs are based on 24 employees working 40-hour weeks for 50 weeks per year. Each employee has an average all-inclusive (salary and fringe benefits) cost per hour of \$32.00, or \$64,000 per year per employee. The total labor cost of \$1,536,000 per year is the same for either option and is independent of utilization.

### 3.2.10.6 Consumables and Supplies

The major costs are for oxygen and coal. The rates per ton of soil are less than those used during the SITE Demonstration because the ratio of soil to coal can be increased during a longer run. Oxygen can be delivered at \$66 tonne (\$60.00/ton) and is expected to be consumed at the rate of 0.83 tonne per tonne of soil. Coal is estimated at \$44/tonne (\$40/ton) and consumed at a rate of 0.353 tonne per tonne of soil. Lime addition at a rate of 0.045

tonne per tonne of soil is estimated to cost \$44/tonne (\$40/ton). SulFerox hydrogen sulfide treatment solvents are estimated to cost \$220 per tonne (\$200 per ton) of sulfur removed or \$5.50/tonne of soil (\$5.00/ton of soil).

### 3.2.10.7 Utilities

The charge for electric power is estimated at a flat rate of \$0.06/kWhr for 447 operating kW (600 operating hp). The water cost is based on \$0.40/1,000 L (\$1.50/1,000 gal) and a consumption rate of 2.5 L/sec (40 gal/min). The cost of utilities for the transportable and control unit were assumed to be equal per ton of soil processed.

### 3.2.10.8 Effluent Treatment and Disposal

This category includes disposal costs for wastewater and the hazardous clarifier bottoms and fine slag — but not syngas or coarse slag whose treatment costs are included in other categories as part of the process. The one-time disposal cost for clarifier bottoms and slag fines was \$250/tonne (\$230/ton) in the SITE Demonstration. The rate for continuing operations should be less. For soil with a dry solids content of 87.7%, of which 62.5% is nonhazardous coarse slag, the disposal of the 30 tonne/day (32 ton/day) hazardous portion at \$220/tonne (\$200/ton) is \$72.40/tonne of soil (\$65.80/ton of soil).

### 3.2.10.9 Residuals and Waste Shipping and Handling

The TGP produces useful by-products. Slag can be sold for the cost of transportation or at no value from a central plant and returned to the site in the transportable unit case. Nonetheless, to be conservative, a cost of \$5.50/tonne (\$5/ton) or \$3.01/tonne of soil (\$2.74/ton of soil) for the coarse slag handling and transport is included for the 62.5% of the solids that is nonhazardous.

The syngas can be valued on a par with natural gas for the transportable unit case and at a higher value for the central plant based on its hydrogen and carbon monoxide content. Syngas is expected to be sold at \$3.30/1,000 kWhr (\$1.00/MM Btu) on-site and at \$6.60/1,000 kWhr (\$2.00/MM Btu) at a central plant. The process equipment to use the syngas is not included in these estimates. The potential uses are as a process fuel or as a feedstock to produce ammonia, methane, or hydrogen.

#### 3.2.10.10 Analytical Services

This category is for sampling and TCLP testing by an independent laboratory on a periodic basis. Tests for lead and several other species, two to four times per day, could be expected to be contracted at a rate of \$60 to \$75 per sample and total \$5.50/tonne (\$5/ton) of waste processed.

#### 3.2.10.11 Maintenance and Modifications

The necessary maintenance can be figured at 3% of the capital cost per year. In previous studies for the Cool Water Coal Gasification Program, the DOE estimated maintenance for the TGP and combined-cycle power plant at 1.5% of capital. The cost at Montebello, including modifications for different configurations, was budgeted at 5% per year.

#### 3.2.10.12 Demobilization

Site demobilization is assumed to cost \$500,000. This is intended to cover all labor and contracts to close and leave a cleanup site. There is no cost assumed for demobilization at the central plant.

### 3.2.11 Design Validation

Each new installation will require a start-up and testing phase which, when performance specifications are met, will validate the design for that unit.

### 3.2.12 Permitting Requirements

The applicable or relevant and appropriate regulations (ARARs) that might apply to the TGP were outlined by US EPA (1995) in its SITE Demonstration Report and include the following:

- RCRA treatment, storage, and land disposal federal regulations (of hazardous waste);
- location-specific ARARs might exist governing construction and operation of the transportable treatment unit and excavation of soils to be treated;
- air quality standards will apply if volatile compounds and particulate emissions occur during excavation, handling, and treatment prior to slurring;

- Clean Water Act regulations govern wastewater discharge to treatment facilities or surface water bodies;
- CERCLA defines drinking water standards established under the Safe Drinking Water Act that apply to remediation of Superfund sites;
- Toxic Substances Control Act prescribes regulations governing the treatment and disposal of wastes containing polychlorinated biphenyls; and
- Occupational Safety and Health Administration requirements apply to CERCLA remedial actions and RCRA corrective actions.

### 3.2.13 Performance Measures

Table 3.5 summarizes the performance of the TGP process based on information reported by US EPA (1995).

### 3.2.14 Design Checklist

Items that must be considered in designing and applying TGP follow:

#### 1. Design Basis

- Volumetric flowrate
- Types of organic contamination in the offgas
- Offgas composition — organics, oxygen, nitrogen, moisture, particulate, and other vapors
- Flowrate and compositional variation
- Chlorine, other halogen, sulfur, and nitrogen contents of any organics
- Organo-phosphorous and metallo-organic concentrations

#### 2. Utility Requirements

- Auxiliary fuel usage
- Electrical usage
- Process water
- Compressed air
- Caustic for neutralizing HCl, other hydrogen halides, and SO<sub>2</sub>

**Table 3.5**  
Evaluation Criteria for the Texaco Gasification Process Technology

Criteria	Performance
Overall Protection of Human Health and the Environment	<ul style="list-style-type: none"> <li>Provides both short and long-term protection by eliminating exposure to both organic and inorganic contaminants in soil.</li> <li>Prevents further groundwater contamination and off-site migration by destroying organic contaminants and demonstrating a potential to immobilize heavy metals into a non-leaching glassy, coarse slag.</li> <li>Requires measures to protect workers and community during excavation, handling and treatment.</li> </ul>
Compliance with Federal ARARs	<ul style="list-style-type: none"> <li>Requires compliance with RCRA treatment, storage, and land disposal regulations (of a hazardous waste).</li> <li>Excavation and construction and operation of on-site treatment unit may require compliance with location specific ARARs.</li> <li>Emission controls are needed to ensure compliance with air quality standards, if volatile compounds and particulate emissions occur during excavation, handling, and treatment prior to slurring.</li> <li>Wastewater discharge to treatment facilities or surface water bodies requires compliance with Clean Water Act regulations.</li> <li>CERCLA defines drinking water standards established under the Safe Drinking Water Act that apply to remediation of Superfund sites.</li> <li>Requires compliance with Toxic Substances Control Act treatment and disposal regulations for wastes containing polychlorinated biphenyls.</li> <li>CERCLA remedial actions and RCRA corrective actions are to be performed in accordance with Occupational Safety and Health Administration requirements.</li> </ul>
Long-Term Effectiveness and Permanence	<ul style="list-style-type: none"> <li>Effectively destroys organic contaminants and demonstrates a potential to immobilize inorganic heavy metals into a non-leaching, glassy, coarse slag.</li> <li>Site contaminants are destroyed or removed with residuals.</li> <li>The potential immobilization of heavy metals into non-leaching, glassy, coarse slag requires further testing for anticipated long-term stability.</li> </ul>

	<ul style="list-style-type: none"> <li>• Fine slag and clarifier solids may require further treatment, particularly when volatile heavy metals are present.</li> <li>• Wastewaters require further treatment to effect long-term stability of contaminants and reuse of water.</li> </ul>
Reduction of Toxicity, Mobility, or Volume Through Treatment	<ul style="list-style-type: none"> <li>• Effectively destroys toxic organic contaminants and demonstrates a potential to immobilize inorganic heavy metals into the primary solid product, a non-leaching glassy coarse slag.</li> <li>• Reduction of soil to glassy slag reduces overall volume of material.</li> </ul>
Short-Term Effectiveness	<ul style="list-style-type: none"> <li>• Emissions and noise controls are required to eliminate potential short-term risks to workers and community from noise exposure and exposure to contaminants and particulate emissions released to air during excavation, handling, and treatment prior to slurring.</li> </ul>
Implementability	<ul style="list-style-type: none"> <li>• Treatability testing required for wastes containing heavy metals.</li> <li>• Large process area required.</li> <li>• Large-scale transportable 100-ton/day unit on multiple transportable skids requires large-scale remediation with on-site commitment of more than 50,000 tons of soil and 2 years of operation.</li> <li>• Initial transportable unit can be constructed and may be available in 24 months.</li> <li>• Large size of unit and ex-situ thermal destruction basis for unit may cause delays in approvals and permits.</li> </ul>
Cost*	<ul style="list-style-type: none"> <li>• Large-scale, complex, high-temperature, high-pressure, transportable thermal destruction unit at approximately \$340/tonne (\$300/ton) of waste soil.</li> </ul>
Community Acceptance	<ul style="list-style-type: none"> <li>• Large-scale, ex situ, high-temperature, high-pressure, thermal destruction unit may require significant effort to gain community acceptance.</li> </ul>
State Acceptance	<ul style="list-style-type: none"> <li>• If remediation is conducted as part of RCRA corrective actions, state regulatory agencies may require operating permits, such as a permit to operate the treatment system, an air emissions permit, and a permit to store contaminated soil for greater than 90 days.</li> </ul>

\*Actual cost of a remediation technology is highly site-specific and dependent on material characteristics.

Source: US EPA 1995

### **3. Regulatory Requirements**

- Air permits
- Wastewater permits

### **4. Site-Specific Considerations**

- Fuel gas (natural gas or liquid propane) availability
- Electrical service
- Wastewater treatment availability
- Wastewater discharge
- Meteorological conditions (wind, lowest temperature)
- Seismic zone
- Distance to the nearest homes, schools, and/or businesses

## **3.3 Flameless Thermal Oxidation**

### **3.3.1 Remediation Goals**

Flameless Thermal Oxidation (FTO) is an innovative technology for the treatment of offgases from Groundwater Air Stripping (GWS) and Solvent Vapor Extraction (SVE) remediation processes. Generally, the offgas from these processes will need treatment to satisfy air quality standards. These air standards vary from state to state and are discussed in more detail in Section 3.3.6.

#### **3.3.1.1 Performance**

In one pilot-scale test program, an FTO supplied by Thermatrix, Inc., San Jose, California, treated a SVE offgas and achieved DEs greater than 99.99% (DOE 1995). A case history for this FTO is presented in Chapter 5. This test involved three full-scale, modular, skid-mounted FTOs with internal heat recovery which were installed in January, 1996, at the Idaho National Engineering Laboratory to treat SVE offgas containing chlorinated volatile organic compounds (CVOCs) from a mixed-waste site. Two of the units are



designed for 680 standard m<sup>3</sup>/hr (400 scfm), and the other is designed for 340 standard m<sup>3</sup>/hr (200 scfm)(DeCicco 1996).

While no data are available for the treatment of the offgas from a GWS system, Thermatrix does have data for the treatment of the offgas from a full-scale industrial wastewater air stripping system. These data show that FTO can achieve DEs of greater than 99.99% (Binder, Woods, and Schofield 1994). Comparable performance when an FTO is applied to pilot- and full-scale groundwater air stripping systems is expected. A case history of the use of FTO in a full-scale industrial wastewater air stripping system is provided in Chapter 5.

As of October, 1995, Thermatrix had installed over 30 FTO units ranging from 1.7 to 11,050 standard m<sup>3</sup>/hr (1 to 6,500 scfm). The 1.7 standard m<sup>3</sup>/hr (1 scfm) units are installed on pump seals for fugitive emission control at a petroleum refinery (Martin, Smythe, and Schofield 1993). The 11,050 standard m<sup>3</sup>/hr (6,500 scfm) unit is installed on an automotive paint finishing booth. Thermatrix has fabricated and delivered a 39,950 standard m<sup>3</sup>/hr (23,500 scfm) unit which had not been placed in service when this monograph was prepared. This unit incorporates three recuperative FTO modules that will be used to treat the offgas from a thermal desorber handling 73 tonne/hr (80 ton/hr) of petroleum contaminated soils. The unit is designed to recover about 60% of the energy in the treated offgas (Wilbourn, Newburn, and Schofield 1994).

Performance data from sources other than SVE or GWS indicate that the FTO is a very efficient emission control device. A 2,125 standard m<sup>3</sup>/hr (1,250 scfm) FTO unit installed as a control device on two American Petroleum Institute (API) separators at a petroleum refinery had a total hydrocarbon (THC) DE of >99.9% and CO concentrations of <10 parts per million by volume (ppmv). A 6,800 standard m<sup>3</sup>/hr (4,000 scfm) FTO unit installed as a control device on a mobile waste oil recovery system had a THC DE of >99.99% and CO concentrations of <10 ppmv. A 5,100 standard m<sup>3</sup>/hr (3,000 scfm) FTO unit installed as a control device for the treatment of non-condensable gases at a pulp mill had a DE of >99.99% for total reduced sulfur compounds and H<sub>2</sub>S concentrations of <5 ppmv. A 2,550 standard m<sup>3</sup>/hr (1,500 scfm), skid-mounted FTO unit installed as a control device at a pesticide production plant had a DE of >99.99% for methylene chloride and other chlorinated hydrocarbon emissions (Wilbourn, Allen, and Baldwin 1995).

The FTO process also produces very low  $\text{NO}_x$  emissions. This occurs because FTO is flameless, and the gases being treated experience a maximum reaction temperature that is near the average temperature. An FTO operating at an average temperature of  $870^\circ\text{C}$  ( $1,600^\circ\text{F}$ ) has a maximum temperature close to  $870^\circ\text{C}$  ( $1,600^\circ\text{F}$ ), not the peak flame temperatures of  $1,650$  to  $1,925^\circ\text{C}$  ( $3,000$  to  $3,500^\circ\text{F}$ ) typically encountered in a conventional thermal oxidizer. This results in typical  $\text{NO}_x$  emissions from FTO of less than 2 ppmv (Binder, Martin, and Smythe 1994). The treatment of nitrogen-containing organics in FTO results in higher  $\text{NO}_x$  concentrations in the stack gas.

### 3.3.1.2 Regulatory and Public Acceptance

Acceptance of FTO by regulatory agencies typically depends on the ability of the technology to meet or exceed air quality standards required at the remediation site. Acceptance of FTO by the public also depends on the ability of the technology to meet or exceed applicable air quality standards, but in some cases will likely involve other issues. These issues, which are sometimes raised when thermal treatment is involved at a remediation site, include questions about the potential for FTO to cause fires, explosions, odors, excessive noise, or emissions such as chlorinated dioxins and furans, which are perceived by the public to be harmful. The FTO process has successfully been permitted in a number of states.

### 3.3.1.3 Reliability

Because FTO is an innovative technology, the technology does not have a long operational history regarding reliability. An analysis of FTO indicates that it has no internal moving parts, has high temperature-resistant and corrosion-resistant ceramic packing, and that the reaction vessel can be constructed of corrosion-resistant alloys (Binder, Woods, and Schofield 1994). These factors and operational data on full-scale FTO units being used for VOC vent control indicate that the technology should be able to operate with reliability factors of 90% or higher. An 8.5 standard  $\text{m}^3/\text{hr}$  (5 scfm) FTO unit operated for a U.S. Department of Energy (DOE) demonstration test, required no maintenance or repairs during a six-week test program (DOE 1995).

### 3.3.2 Design Basis

The overall design basis of GWS or SVE systems provides the data necessary to evaluate different offgas treatment technologies, such as carbon absorption, conventional thermal oxidation, catalytic oxidation, and FTO. This comparative evaluation is used to select the most appropriate offgas treatment technology based on performance, economics, and site-specific considerations. The key factors needed to evaluate FTO as a gas treatment technology are described in the following subsections.

#### 3.3.2.1 Volumetric Flowrate

The volumetric flowrate of the offgas from the GWS or the SVE system should be estimated. The minimum and maximum flowrates and the flowrate variability during normal operation and over the project's life are also necessary.

#### 3.3.2.2 Organic Concentrations

The organic concentration in the offgas from the GWS or the SVE system should be estimated. The minimum and maximum organic concentrations and the organic concentration variability during normal operation and over the project's life should also be estimated. If the offgas contains more than  $267 \text{ kcal/m}^3$  ( $30 \text{ Btu/ft}^3$ ), the oxidation reaction is self-sustaining, and no auxiliary fuel or recuperative heat exchange would be necessary in the FTO design (Binder and Martin 1993). For offgas with a lower organic concentration, internal heat recovery can be built into the reactor (Wilbourn, Allen, and Baldwin 1995), thereby producing a self-sustaining reaction down to less than  $89 \text{ kcal/m}^3$  ( $10 \text{ Btu/ft}^3$ ) (Martin, Woods, and Schofield 1994). At very low concentrations, even with recuperative air preheat, auxiliary fuel usage might be high enough to consider using an organic concentration technology as an offgas pretreatment. Organic concentration devices have been developed, using carbon or zeolites, that can increase organic concentrations and reduce volumetric flowrates by a factor of ten or more (Anonymous 1992). The incorporation of an organic concentrator in the design must be carefully evaluated, however, relative to the increased potential for explosions, since the concentrated organic could be above its Lower Explosive Limit (LEL).

An important design consideration with SVE systems is that the concentration of organic in the air will decrease over time as the organic is volatilized from the soil (Johnson et al. 1994). This will impact auxiliary fuel usage and the possible need for recuperative heat exchange; these needs must be reflected in the FTO design.

### 3.3.2.3 Types of Organic

The FTO process can treat most types of organics that occur as contaminants at remediation sites. Table 3.6 lists some of the compounds that have been treated by FTO.

If chlorinated, halogenated, or sulfur-containing organics are present in the GWS or SVE offgas, wet scrubber pretreatment of the reactor offgas may be required by US EPA or state regulatory agencies. Chlorinated or sulfur-containing compounds in a wet or very humid offgas feed to an FTO could also result in the need for special alloys for the construction of the reactor vessel. For example, a 170 standard m<sup>3</sup>/hr (100 scfm) full-scale FTO, which is treating the offgas from a wastewater air stripper containing chlorinated organics, is constructed of a chromium-nickel-aluminum alloy (Binder, Woods, and Schofield 1994). Carbon steel lined with protective resins can also be used when corrosive gases are being treated. The FTOs being used at the Idaho National Engineering Laboratory are constructed of carbon steel lined with Siloxirane (DeCicco 1996).

The presence of organo-phosphorous and metallo-organic compounds in the SVE or GWS offgas would also need to be considered in design development. Oxidation of these compounds in an FTO might generate a solid inorganic particulate that could condense into a solid residue and plug the ceramic packing (Martin, Woods, and Schofield 1994). Metallo-organics containing high vapor pressure inorganics, such as mercury and certain forms of arsenic, would have low plugging potential at reaction temperatures and could probably be treated in the unit if a suitable air pollution control system were incorporated into the system design. If there are uncertainties about the plugging potential of a particular metallo-organic compound in an FTO, pilot testing should be used to assess the suitability of the technology.

**Table 3.6**  
Compounds Processed by Thermatrix FTO

Petroleum Fuel Hydrocarbons	Sulfonated	Aromatics/Cyclics	Nitrogenated	Halogenated	Others
Methane	Hydrogen Sulfide	Benzene	Ammonia	Methyl Chloride	Isopropanol
Propane	Methyl Mercaptan	Toluene	Monomethylamine	Dichloromethane	Methanol
Hexane	Dimethyl Sulfide	Xylene	Dibutylamine	Chloroethane	Acetone
Heptane	Dimethyl Disulfide	Pinene		Trichloroethane	Methyl Ethyl Ketone
Octane		Polychlorinated Biphenyls		Trichloroethylene	Acrylic Acid
Naphtha				Perchloroethylene	Formaldehyde
JP-5 Jet Fuel				Chloroform	Methyl Tert-Butyl Ether
				Carbon Tetrachloride	Dichloromethyl Ether
				Freon	Hexamethyldisilazane

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### 3.3.2.4 GWS or SVE Offgas Composition

The particulate concentration of the offgas from the GWS or SVE system should be estimated, as well as the minimum and maximum particulate concentration variability during normal operation and over the project's life. The particulate concentrations in the GWS or SVE offgas stream need to be very low to minimize plugging of the reactor bed. If necessary, this can be accomplished by prefiltering the GWS or SVE offgas.

The moisture content of the offgas from the GWS or the SVE system should be estimated. The variability of the moisture content during normal operation and over the project's life should also be gauged. The offgas from most GWS and from some SVE systems is saturated with moisture. Condensation of this moisture in the ductwork leading to the FTO needs to be considered in the design.

### 3.3.2.5 Utility Requirements

Process utility requirements — auxiliary fuel, electricity, water, and compressed air — should be estimated as part of the design. The auxiliary fuel requirements of the FTO can be estimated using a mass-energy balance. Other utility requirements are available from Thermatrix since they may be technology-specific and difficult to estimate.

### 3.3.2.6 Regulatory Basis

The US EPA and/or state regulatory requirements for the offgas treatment system are a very important part of the design. These air quality standards vary from state to state and can involve some or all of the following:

- minimum DE, based on a stack test, of specific organic contaminants in the SVE or GWS offgas;
- maximum concentration, based on a stack test, of specific organic contaminants in the treated exhaust gas;
- maximum organic mass emission rate, based on a stack test, of specific organic contaminants in the treated exhaust gas;
- maximum nitric oxide ( $\text{NO}_x$ ) concentration in the treated exhaust gas, generally based on testing; and

- maximum particulate, HCl, and/or SO<sub>2</sub> concentrations in the treated exhaust gas from the posttreatment wet scrubber, generally based on testing.

While it is common to require CO and/or THC continuous emissions monitors (CEMs) on the exhaust gas of a conventional thermal oxidizer during an SVE or GWS related remediation, CEMs have never been required by a state regulatory agency for any FTO air permits. The most common FTO operating permit condition is an automatic low temperature waste gas cutoff (DeCicco 1996).

### 3.3.2.7 Pilot Test Data

Bench-scale or pilot-scale data can serve as inputs to design to confirm that the FTO can meet the regulatory requirements for organic destruction, organic emissions, THC, CO, and NO<sub>x</sub>. Thermatrix has a 1.7 standard m<sup>3</sup>/hr (1 scfm) bench-scale unit and an 8.5 standard m<sup>3</sup>/hr (5 scfm), skid-mounted pilot unit available for field testing on slip-streams of offgas from GWS or SVE projects.

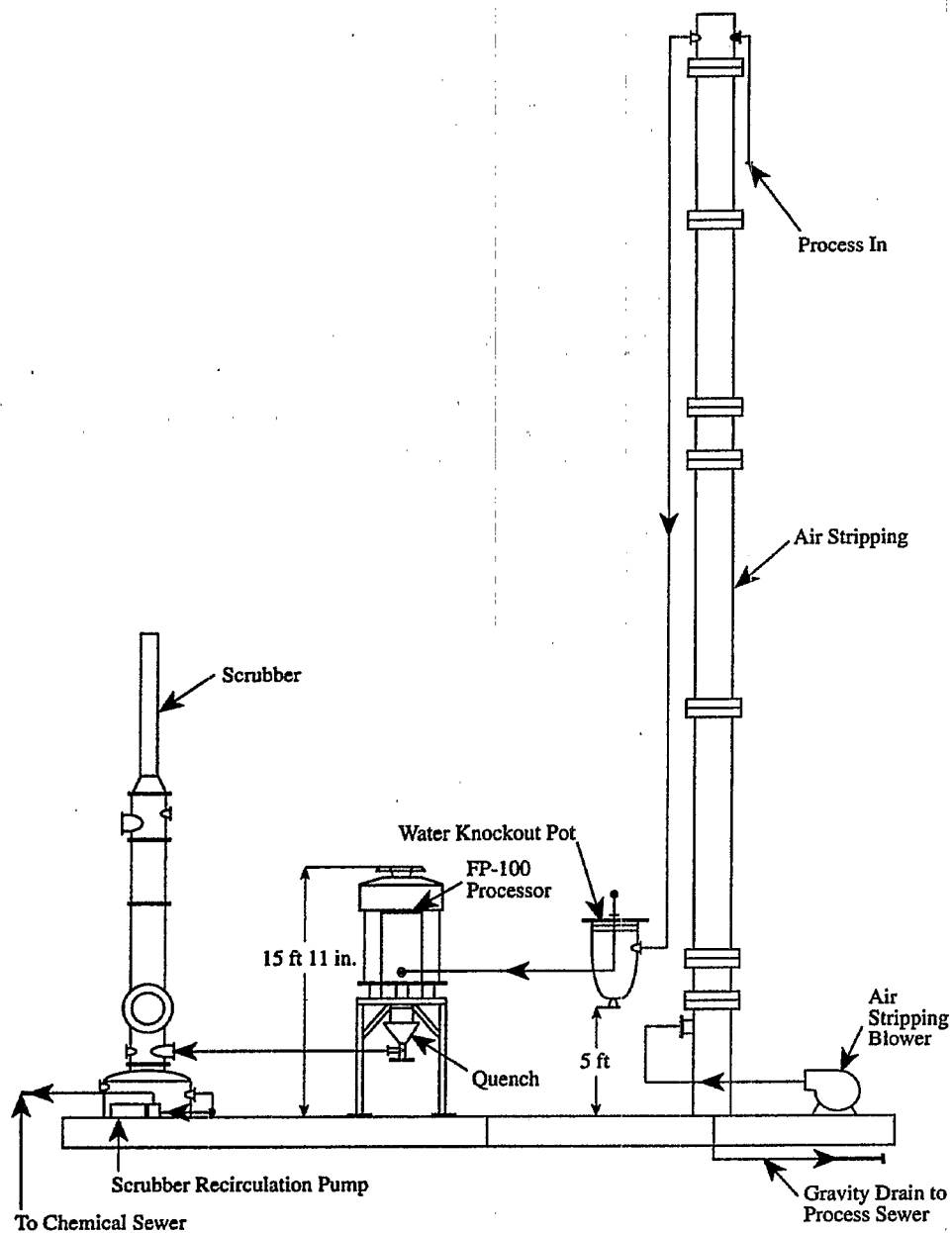
### 3.3.3 Design and Equipment Selection

The design basis information is used to develop a duty specification that would be used to solicit a bid on the supply of the equipment to treat the SVE or GWS offgas. A typical equipment layout for FTO treating GWS offgas is shown in Figure 3.3. A typical process-flow diagram for FTO treating SVE offgas is shown in Figure 3.4.

### 3.3.4 Process Modifications

During design development, consideration should be given to the impact of variable or changing site conditions. For an SVE process, contaminant concentrations in the soil can vary significantly from one area to another. In addition, during operation, the contaminant present in the offgas will gradually decline as the contaminant is vaporized from the soil. Variable soil contaminant concentrations should be addressed during the soil investigation and accounted for in FTO design by using a realistic upper limit for the contaminant concentration. A reasonable balance must be reached however, between capital cost and equipment flexibility. Declining contaminant concentrations in the SVE offgas can also be accommodated by having

**Figure 3.3**  
Thermatrix FTO Treatment System — Wastewater Stripper Offgas

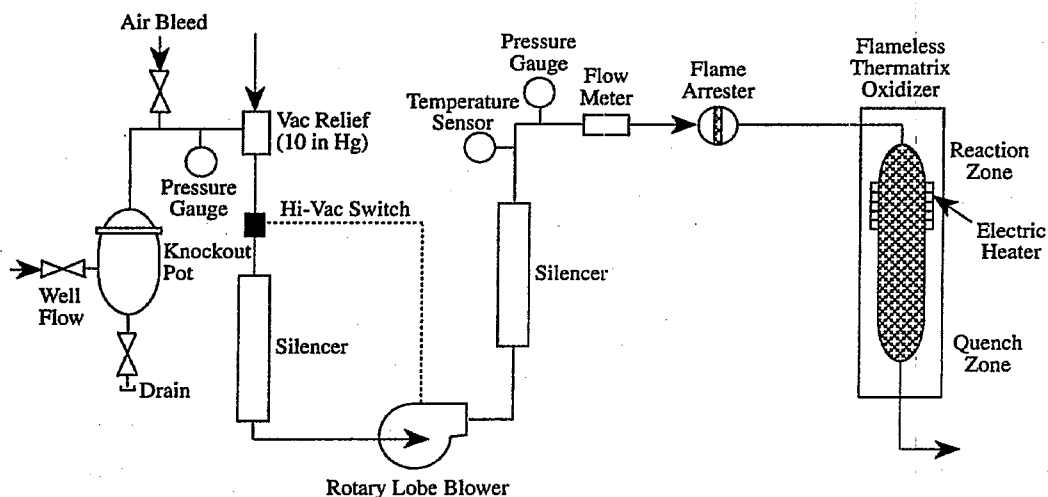


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**Figure 3.4**

Process-Flow Diagram of Thermatrix FTO Treating SVE Offgas



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sufficient auxiliary fuel capability to ensure complete destruction. Spikes of high concentration volatile organic compounds (VOCs), while not common in SVE applications, can be handled by the FTO design (DeCicco 1996). Since the FTO can be skid- or trailer-mounted, the process can be easily modified by adding equipment.

### 3.3.5 Pretreatment Processes

In GWS and SVE systems in which entrainment of liquid water droplets can occur, the offgas should pass through a knock-out pot followed by a flame arrestor and a mist eliminator. Such offgas pretreatment minimizes impingement of droplets of entrained and condensed liquid water on the hot packing in the reaction zone. The flame arrestor is a safeguard against flash-back to potentially explosive mixtures in the knock-out pot headspace.

### 3.3.6 Posttreatment Processes

If the organic contaminants in the offgas from a GWS or SVE system contain only carbon, hydrogen, and oxygen, then it is likely that the FTO exhaust gas can go directly to the atmosphere without any posttreatment. However, if the organic contaminants contain other elements, such as halogens or sulfur, then a posttreatment system, such as a packed-bed alkaline wet scrubber, might be required to remove acid gases, such as HCl, other hydrogen halides, or SO<sub>2</sub>. The need for a posttreatment wet scrubber depends on the concentration of the acid gases in the FTO offgas, and any US EPA and/or state regulatory performance or emission standards that are part of the site-specific remediation agreements at the site. Additional treatment or permitting can be required for the scrubber wastewater that contains salts. The degree and type of scrubber wastewater permitting and/or treatment depends on site-specific considerations and US EPA and/or state regulatory effluent and treatment standards that are part of the site-specific remediation agreements.

### 3.3.7 Process Instrumentation and Controls

For either an SVE system or a GWS system, the key instruments are the blower flow meter and the FTO temperature indicator. While LEL meters and stack CEMS are generally not required (DeCicco 1996), some state regulatory agencies require them.

### 3.3.8 Safety Requirements

It is common practice to use an LEL meter on any offgas entering a thermal control device if the offgas contains organics at concentrations which can potentially exceed the LEL. Extensive testing by Fenwall Safety Systems Co. showed that the heat capacity and geometry of the ceramic packing matrix provides an inherent flame arresting capability (Woods, Binder, and Schofield 1994). A 1.7 standard m<sup>3</sup>/hr (1 scfm) FTO unit was tested at an engineering safety laboratory at organic concentrations from 5% of the LEL up to 170% of the upper explosive limit (UEL). Under all test conditions, there was no evidence of flashback, detonation, or any uncontrolled combustion (Martin, Smythe, and Schofield 1993). However, a Hazardous Operation (HAZOP) analysis should be considered to determine whether an LEL meter and flame arrestors need to be incorporated into the design and operation of an FTO.

### 3.3.9 Specification Development

Because the discussions in this section are only considered to be guidance, it is important to discuss with the SVE or GWS equipment suppliers whether there are any site-specific or other factors that must also be considered during the development of the procurement specification.

The procurement specification should incorporate the considerations discussed in the Design Basis, Section 3.3.2. The key procurement specifications for either an SVE or GWS treatment system include the following:

- volumetric flowrate;
- types of organic contamination in the offgas;
- offgas composition:
  - organics,
  - oxygen,
  - nitrogen,
  - moisture,
  - particulate,
  - other vapors;
- flowrate and compositional variation;
- chlorine, other halogens, sulfur, and nitrogen contents of any organics; and
- organo-phosphorous and metallo-organic concentrations.

A performance test is often developed and included with the procurement specification. Acceptance of the final system can be contingent on the system passing the performance test.

### 3.3.10 Cost Data

A demonstration test was conducted at the DOE's Savannah River Integrated Demonstration site using the FTO to treat the offgas from an SVE system (DOE 1995b). In its summary report, the DOE provided a cost estimate for a 680 standard m<sup>3</sup>/hr (400 scfm), gas-fired FTO treating SVE offgas. A cost estimate for an FTO system of the same size to treat an SVE offgas containing an average of 400 ppmv of chlorinated volatile organic

compound (CVOC) or 1.7 kg (3.7 lb) of CVOC per hour was prepared using information from the DOE report, discussions with Thermatrix, and the authors' experience. That cost estimate is summarized in Table 3.7 and includes the following assumptions:

- FTO has an operating factor of 95% or 8,322 hr/yr (DeCicco 1996);
- installed capital cost of a 680 standard m<sup>3</sup>/hr (400 scfm), skid-mounted recuperative style FTO unit is \$160,000;
- capital recovery at 10% for seven years (capital recovery factor of 0.2089)(authors' experience);
- one operator per shift for four shifts at \$40,000 per year with 20% of each operator's time dedicated to the FTO unit (DeCicco 1996 and authors' experience);
- one supervisor at \$60,000 per year and 20% of the supervisor's time dedicated to the FTO unit (DeCicco 1996 and authors' experience);
- maintenance costs based on 3% of installed capital per year (authors' experience);
- auxiliary gas cost of \$6,920 per year for 315,000 Btu/hr; and
- power costs of \$530 per year.

The estimate does not include the capital and operating costs for a wet scrubber. If a wet scrubber for the removal of acid gases such as HCl is required, the costs for this operation would need to be added.

### 3.3.11 Design Validation

Validation of the process can be accomplished by including a performance test with the procurement specification. In this instance, acceptance of the final system is contingent upon the system passing the performance test. A peer review during the procurement and design process is another commonly used design validation method that could be applied to FTO.

### 3.3.12 Permitting Requirements

Prior to the procurement of equipment, the US EPA and/or state regulatory agencies need technical and performance information on FTO pertaining to the offgas treatment system's ability to comply with air quality requirements. This

**Table 3.7**  
**Process Cost Estimate of a FTO Treating SVE Offgas**

Process Operating Costs	Cost (\$/yr)	\$/kg CVOC	\$/lb CVOC
Labor	\$44,000	\$3.14	\$1.43
Auxiliary Fuel	\$6,920	\$0.49	\$0.22
Power	\$530	\$0.04	\$0.02
Maintenance @ 3% of Capital	\$4,800	\$0.34	\$0.16
<b>Operating Costs-Sub Total</b>	<b>\$56,250</b>	<b>\$4.02</b>	<b>\$1.83</b>
Capital Recovery	\$33,420	\$2.39	\$1.09
<b>Total Process Costs</b>	<b>\$89,670</b>	<b>\$6.41</b>	<b>\$2.91</b>

Capital Cost (1995) = \$160,000

Source: DOE 1995b

technical information typically involves a description of the FTO process, a conceptual design showing the preliminary process, and performance data from similar installations. After approval of FTO for the application, the state and US EPA will probably want to review more detailed information, such as process-flow diagrams (PFDs) and piping and instrument diagrams (P&IDs) during the procurement and installation phase. If relevant bench-scale or pilot-scale data are available, the state and US EPA will also want to examine these data to confirm that FTO can meet state and/or US EPA requirements.

The air quality standards vary from state to state and can involve some or all of the following:

- minimum DE, based on a stack test, of specific organic contaminants in the SVE or GWS offgas;
- maximum concentration, based on a stack test, of specific organic contaminants in the treated exhaust gas;
- maximum organic mass emission rate, based on a stack test, of specific organic contaminants in the treated exhaust gas;
- maximum nitric oxide ( $\text{NO}_x$ ) concentration in the treated exhaust gas, generally based on testing; and

- maximum particulate, HCl, and/or SO<sub>2</sub> concentrations in the treated exhaust gas from the posttreatment wet scrubber, generally based on testing.

While it is common to require CO and/or THC CEMS on the exhaust gas of a conventional thermal oxidizer during an SVE or GWS related remediation, CEMS have never been required by a state regulatory agency for any FTO air permits. The most common FTO operating permit condition is an automatic low temperature, waste gas cutoff (DeCicco 1996). Other permitting areas not listed above, such as metal emissions, could be required. Special requirements, such as radionuclide emission regulations, could also be required for DOE sites.

### 3.3.13 Performance Measures

Performance measurements that are required for FTO by states and US EPA vary from state to state. For projects involving SVE or GWS offgas treatment, performance measurements generally incorporate the state air permit requirements for an organic emission control device. Some of the possible performance measurements are:

- Destruction efficiencies for either total hydrocarbons or specific constituents, such as dichloroethane, may be required. The DE requirements could range from 95% to 99.99% depending on the state and the specific constituents in the offgas. Many states have maximum ground level concentration standards that require dispersion calculations based on stack concentrations of specific organic constituents;
- Hydrogen chloride removal efficiencies of 99% or emissions of less than 4 lb/hr out the stack could be required; and
- Depending on the state, SO<sub>2</sub> and/or NO<sub>x</sub> emissions might be regulated.

It has been Thermatrix's experience that CEMS for CO, THC, HCl, NO<sub>x</sub> and SO<sub>2</sub> have never been required by regulatory agencies for air permits (DeCicco 1996). Other performance measures, not listed above, such as metal emissions, could be required. Special requirements, such as radionuclide emissions could also be required for DOE sites.

### 3.3.14 Design Checklist

The key factors that must be considered when procuring and installing FTO are summarized in the following checklist:

#### 1. Design Basis

- Volumetric flowrate
- Types of organic contamination in the offgas
- Offgas composition — organics, oxygen, nitrogen, moisture, particulate, and other vapors
- Flowrate and compositional variation
- Chlorine, other halogens, sulfur, and nitrogen contents of any organics
- Organo-phosphorous and metallo-organic concentrations

#### 2. Utility Requirements

- Auxiliary fuel usage
- Electrical usage
- Process water
- Compressed air
- Caustic for neutralizing HCl, other hydrogen halides, and SO<sub>2</sub>

#### 3. Regulatory Requirements

- Air permits
- Wastewater permits

#### 4. Site-Specific Considerations

- Fuel gas (natural gas or liquid propane) availability
- Electrical service
- Wastewater treatment availability
- Wastewater discharge
- Meteorological conditions (wind, lowest temperature)

- Seismic conditions
- Distance to the nearest homes, schools, and/or businesses.

Special requirements, such as radionuclide emissions, could also be required for DOE sites.

### **3.4 Plasma Furnaces**

The process developed by the Exide Corporation and commercially-available through Asea Brown Boveri (ABB). There are many types of plasma furnaces and many types of designs that differ significantly in chamber configuration (fixed/table), electrode configuration, arc type, cooling system, electrode type, power (AC/DC), and other design elements. The process was chosen to illustrate the application of plasma furnaces

The Exide Corporation process uses plasma arc technology originally developed by ABB. Commercial systems supplied by ABB are operating in Europe and South Africa (since the mid 1980s), using controlled atmosphere and hollow electrode feed systems. In the early 1990s, South Carolina Research Authority operated a research unit in Charleston with the ABB technology.

#### **3.4.1 Remediation Goals**

In July 1992, the US EPA issued a Record of Decision (ROD) for remedial action at a former used battery recycling site. The US EPA's strategy for cleaning up the site included innovative thermal treatment technology to treat soil contaminated with battery casings and lead.

To meet US EPA's goals, the Exide Corporation conducted a two-phase pilot program to evaluate the feasibility of using their plasma furnace technology. This technology was specifically developed to treat soils associated with secondary battery smelting operations that contain broken battery cases and separator plates containing a variety of organic and chlorinated organic compounds, as well as lead, lead sulfate, and associated metal compounds. It is a high temperature process which introduces the liquid, solids smaller than 1.6 cm (5/8 in.), and gaseous wastes directly into the plasma zone of the furnace by means of a hollow electrode. Larger



solids, not introduced through the electrode, can be added through air-locks in the roof of the furnace.

The goals for the plasma furnace process are to produce clean, combustible synthesis gas, a molten ceramic slag that passes US EPA's Toxic Leaching Characteristic Procedure (TCLP), and metal for recycle. Since the furnace uses electrical power to drive the reactions, the process creates minimum quantities of effluents (solid, liquid, or gas).

### 3.4.2 Design Basis

The primary objective of the plasma furnace process is to remove the maximum amount of lead from the feed and to render the trace amount of lead that is not removed into an insoluble form, as measured by TCLP. A secondary objective is to optimize the use of chemical energy from the battery case materials so as to minimize the cost of operation.

#### 3.4.2.1 Post Combustion Ratios

The effectiveness of heat transfer from the plasma and the chemical reactions to the feed materials depends on the geometry and the temperature differential between the plasma and the material being heated. Since more energy is generated by converting carbon to  $\text{CO}_2$  than by converting carbon to  $\text{CO}$ , sufficient oxygen is needed for conversion to  $\text{CO}_2$  to maximize the use of chemical energy in the furnace. It should be noted that a graphite electrode is also susceptible to oxidation reactions. This becomes less critical if a reducing offgas with a high  $\text{CO}$  content can serve as an energy source for another process.

The degree to which combustion reactions have proceeded to completion ( $\text{CO}_2$  and  $\text{H}_2\text{O}$ ) is typically measured as the post combustion ratio (PCR). There are two ways to express the PCR using volumetric gas composition measurements:

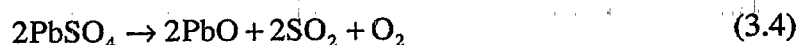
$$\text{PCR} = \frac{\text{CO}_2}{(\text{CO}_2 + \text{CO})} \quad (3.2)$$

$$\text{PCR} = \frac{(\text{CO}_2 + \text{H}_2\text{O})}{(\text{CO}_2 + \text{H}_2\text{O} + \text{CO} + \text{H}_2)} \quad (3.3)$$

As Equation 3.2 requires only CO<sub>2</sub> and CO volumetric concentration measurements, it is somewhat simpler to measure and lends itself to continuous monitoring.

### 3.4.2.2 Theoretical Fuming Rate

A production system is designed to operate at temperatures exceeding 1,649°C (3,000°F) to maximize the vaporization of lead. Lead sulfate in soils fed to the furnace decomposes to lead oxide according to the equation:



Lead metal entering the furnace can be oxidized to lead oxide according to:



and, if reducing conditions are maintained, lead oxide can be reduced according to the reverse of Equation 3.5. The vapor pressure of lead (Brimacombe 1989; Jacob and Toguri 1975; Holl 1989; Willis 1980; Toop 1994), as a function of temperature, is:

$$\log P = -\frac{10,130}{T} + 8.28 - 0.985 \log T \quad (3.6)$$

and for lead oxide, as a function of temperature, is:

$$\log P = -\frac{10,598}{T} + 6.012 \quad (3.7)$$

Lead in the furnace converts to liquid phase and vaporizes at a rate that is dependent on both temperature and gas flow conditions (Kellogg 1967; Richards and Brimacombe 1985). Lead that volatilizes is carried out of the furnace with the offgas, condensing to liquid and solid phases. The lead that leaves the furnace with the offgases is referred to as fume. As the fume cools, it can collect as deposits on furnace ductwork or be captured by the offgas particulate collection system. The lead-bearing capacity of the offgas limits the fuming rate of the furnace. For optimal lead removal, the theoretical fuming rate must exceed the lead introduction rate. A theoretical fuming rate can be calculated as follows:

$$P_{Pb} = \frac{(M_{Pb})}{(M_{Pb} + M_{offgas})} \quad (3.8)$$

where:  $P_{Pb}$  = vapor pressure of lead at temperature T;  
 $M_{Pb}$  = moles of lead fumed per hour; and  
 $M_{offgas}$  = moles of offgas generated per hour.

Using 207 as the molecular weight for lead, and solving Equation 3.8, the theoretical fuming rate (TFR) is:

$$TFR = 207M_{Pb} = \frac{M_{offgas}P_{Pb}}{(1 - P_{Pb})} \quad (3.9)$$

### 3.4.3 Design and Equipment Selection

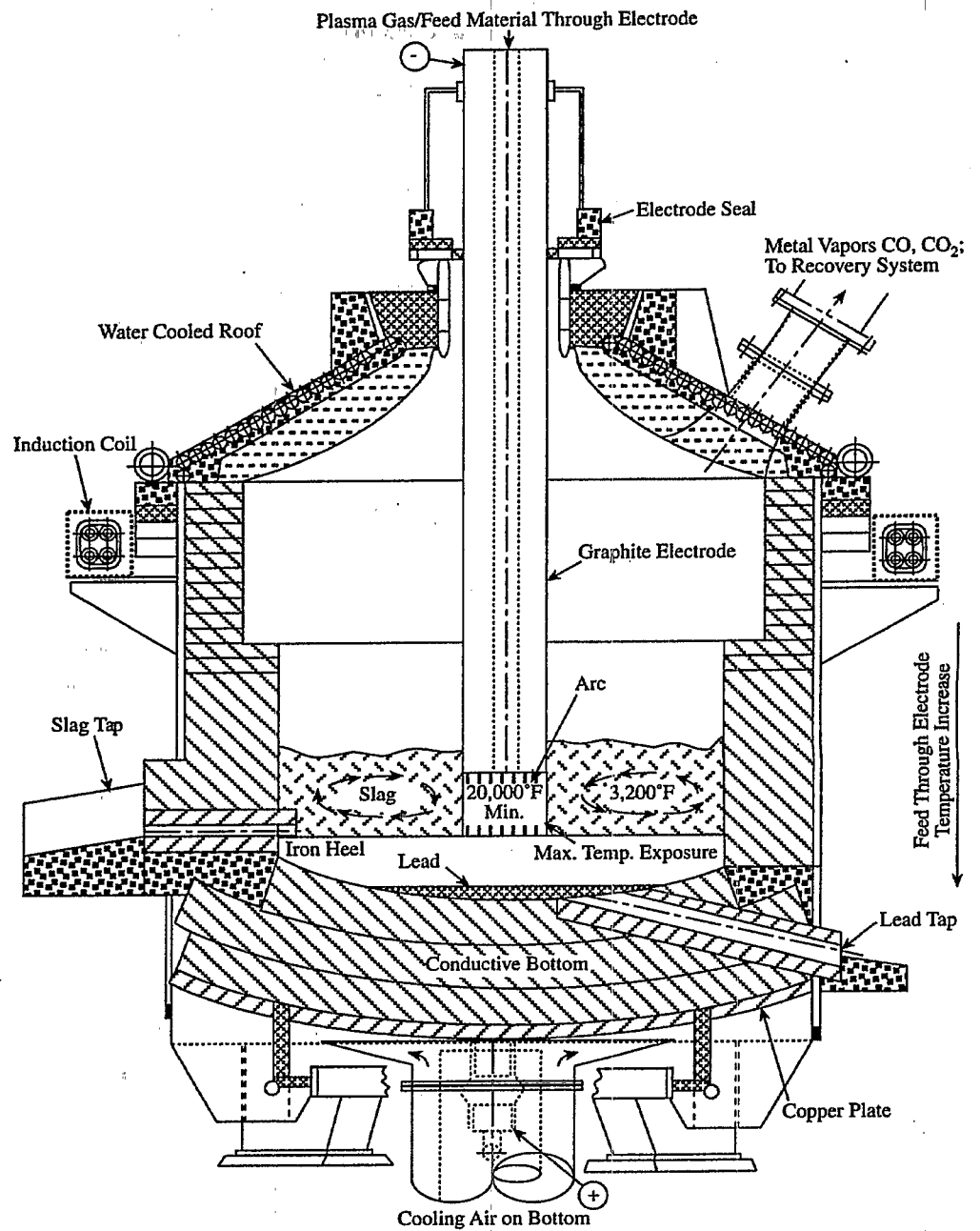
The plasma furnace used by the Exide Corporation is a direct current arc furnace with a refractory-lined chamber; a side elevation of the furnace is shown in Figure 3.5. It has an air-cooled bottom, with an electrical connection and a copper plate to distribute the current evenly over the bottom. Refractories in the bottom of the furnace are electrically conductive.

The graphite electrode can be moved up and down to compensate for changes in the bath depth as materials build up in the slag or metal phases or as the slag or metal are tapped from the furnace. The movement also compensates for any electrode consumption. The electrode position determines the arc length and, thus, the operating voltage. The hollow electrode is proven technology. Commercial graphite electrodes are available from several companies in sizes up to 91.44 cm (36 in.) in diameter. Electrodes cost approximately \$1 to \$2 per pound, depending on the custom machining requested, and are available in many lengths and diameters. They usually have tapered threaded ends to join sections together; however, the furnace must be de-energized to add an electrode section.

The roof of the furnace is water cooled and helps to guard the furnace from electrical short circuits formed through the layer of frozen metal. Not shown in Figure 3.5 is an auxiliary opening in the roof that can be used to charge larger pieces into the furnace.

An induction coil circling the furnace helps to stir the bath and confine the plasma zone, in addition to the natural arc pressure. The plasma zone of

**Figure 3.5**  
Plasma Furnace Cross-Section



Reproduced courtesy of Exide Corp.

the furnace is below the electrode, and the freeboard area, or furnace atmosphere, is above the bath.

Plasma support gas is added to the furnace through the hollow electrode and ends up as part of the furnace atmosphere. Any of several gases can be used. In the laboratory, argon or helium is frequently used. Reducing gases, such as  $H_2$  or CO work as plasma support gases. When the substances being treated contain significant amounts of organic chemicals, the furnace freeboard is soon dominated by  $H_2$  and CO. The freeboard volume of the furnace is relatively large, and the exhaust gas volumes are small, so residence time in the furnace is long and the space velocities are low. Particulates are less easily entrained and swept from the furnace. The furnace atmosphere is maintained at a slightly negative pressure. Plasma arc furnaces for hazardous waste management are procured as a unit; they are not designed per se. Other suppliers of plasma arc furnaces have designs similar to ABB.

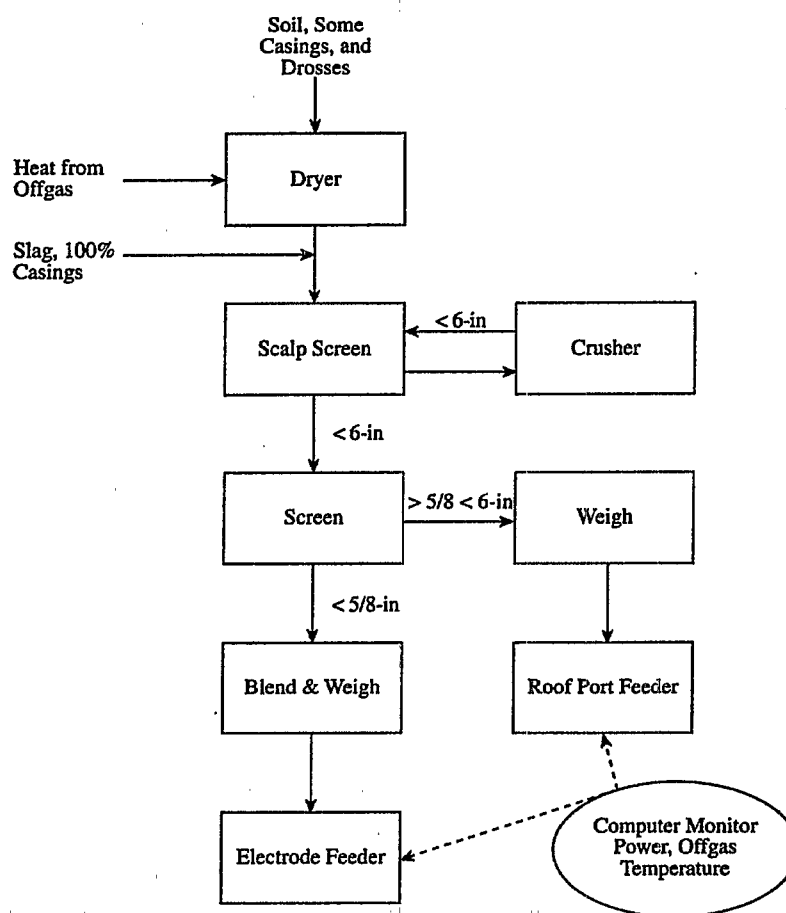
#### 3.4.4 Process Modifications

Depending on site-specific considerations, energy recovery from plasma arc furnaces can be modified to provide methanol conversion, hydrogen conversion, or cogeneration. Also refer to the Section 3.4.6, Posttreatment Processes.

#### 3.4.5 Pretreatment Processes

Solids are mixed and blended to obtain uniform composition prior to their introduction into the furnace. During pilot tests, the feed material was sized to minus 0.9525 cm (0.375 in.), so that it could pass unobstructed down the 5.08 cm (2 in.) diameter hollow electrode. With a larger electrode, handling pieces up to 2.54 cm (1 in.) should be possible. Figure 3.6 shows the solids feed system used in the 1994 battery site cleanup tests. A vibrating screw feeder with a variable speed drive is mounted on a load cell to meter the rate of solids delivered to the furnace. A feed pipe with a rotary feeder and isolation valve conveys solids into the hollow electrode. The excavated contaminated soil is bedded or blended for compositional uniformity and is usually dried ahead of the furnace.

**Figure 3.6**  
Solids Preprocessing and Feed System

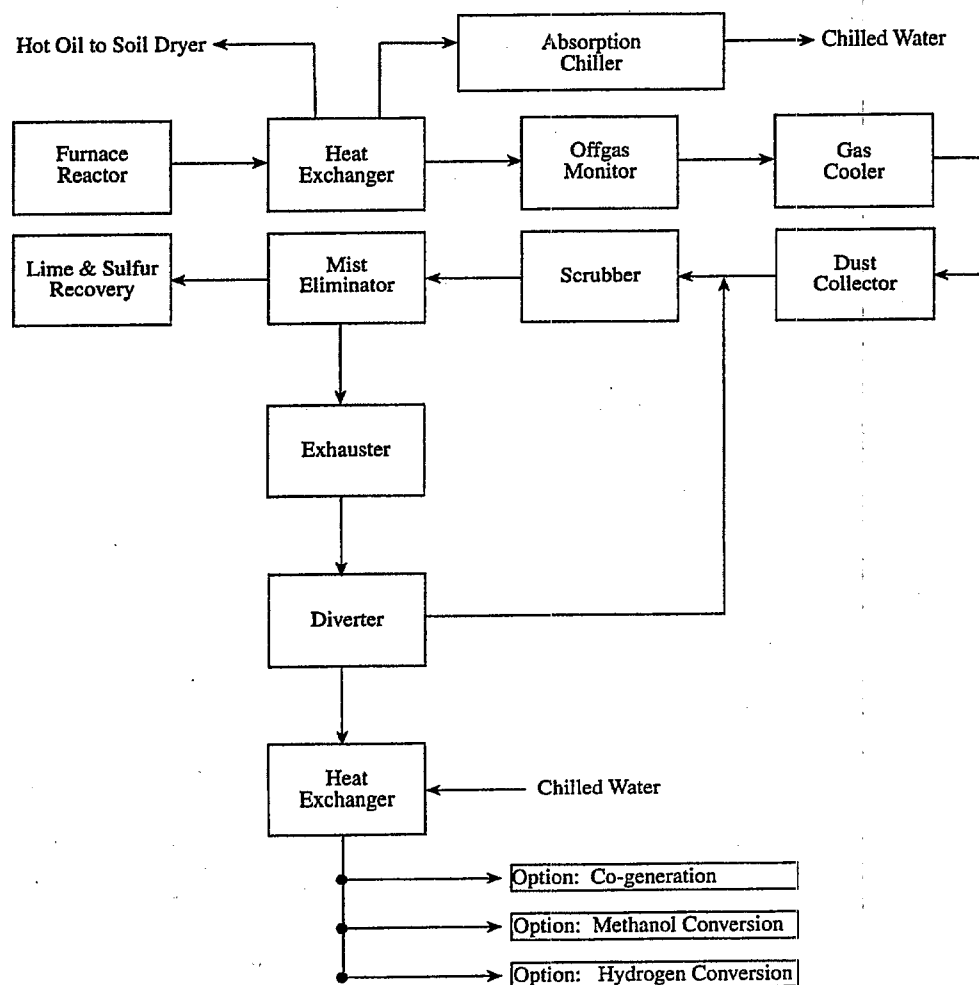


### 3.4.6 Posttreatment Processes

Plasma furnaces use conventional wet and/or dry air pollution control systems. The volume of offgas produced by plasma furnaces is minimal, since they use electric power to establish the high temperature environment which drives thermal destruction.

Exide's recommended offgas tempering and cleaning system (assuming 5% or less carbon content in the feed materials) is shown in Figure 3.7. Synthesis gas from the furnace enters an optional afterburner where the addition of oxygen (or air) liberates heat for recovery. Gases from the afterburner are cooled prior to entering a fabric filter. The fabric filter removes particulates. Depending on the material being treated, acid gases can be removed in a wet

**Figure 3.7**  
Offgas Cleanup System with Energy Recovery



reflux, or other type of scrubbing system. Feed containing greater than 5% carbon can produce a high Btu synthesis gas that has potential for further chemical conversion or cogeneration.

Metals, such as iron or copper, are reduced and recovered as liquid metal. This type of furnace has been used to metallurgically process ferro-chromium, ferro-nickel, ferro-silicon, and other metal alloys. They enter the furnace as oxides or natural ores and are recovered as metals. Contaminated soils, as are natural ores, are melted to form slag. Slag, withdrawn from the furnace at approximately 1,760°C (3,200°F), when solidified, has a density greater than 3,200 kg/m<sup>3</sup> (200 lb/ft<sup>3</sup>).

### **3.4.7 Process Instrumentation and Controls**

The plasma furnace instrumentation and controls consist of DC power supply controls and a means of tapping the furnace periodically to remove and recover accumulated metal and slag. Power supply technology for high amperage rectification is commercially available. The graphite electrode can be moved up and down to compensate for changes in pool depth as materials build up in the slag and metal phases or as slag and metal are tapped from the furnace.

Since the plasma furnace operates in a reducing atmosphere and produces a combustible gas, common practice is to use instrumentation to detect the LEL in the furnace offgas.

### **3.4.8 Safety Requirements**

An operational hazards evaluation should be conducted on a site-by-site basis to identify potential hazards associated with the plasma furnace system and specific waste feed materials. The following section discusses general safety issues. However, the system operator should analyze each project to identify and develop plans for dealing with site-specific situations.

A number of standard safety precautions are required and should be observed. All systems must comply with Occupational Safety and Health Act (OSHA) requirements. These include, but are not limited to, confined space entry procedures, fire protection, and spill protection. Precautions relating to hot operating equipment, such as warning signs, barriers, and safety shields, must be implemented. Conveyors and other



mechanical and electrical equipment must have adequate lock-out/tag-out safety mechanisms to prevent inadvertent operation during maintenance. Special attention to high voltage electrical safety precautions are required. Special precautions must also be observed to contain the withdrawn slag so as to avoid fires and personnel injury.

In addition to the safety of personnel and equipment, environmental safety is also a key consideration. Monitoring of the LEL in the offgas and the proper fracturing of system controls ensures the protection of the surrounding environment.

### 3.4.9 Specification Development

A specification package couples the characteristics of the contaminated materials requiring treatment with the design specifications available for plasma furnaces. As an example, some procurement specifications might be:

- size reduction requirements for the contaminated soil entering the furnace;
- moisture content or drying requirements for the contaminated soil;
- organics concentrations in the contaminated material;
- metals concentrations in the contaminated soil;
- capacity of plasma furnace to treat contaminated soil;
- volumetric flow rates into and out of the furnace;
- offgas composition, including organics, metals, oxygen, moisture, particulate, nitrogen, and other vapors;
- frequency for tapping metal and slag from the furnace;
- offgas cleaning requirements;
- process control requirements;
- electricity costs; and
- desired offgas utilization — cogeneration, methanol, hydrogen, etc.

To verify that the final facility meets the specification package, an acceptance test should be included. Ownership of the facility should be made contingent on the facility's ability to pass the acceptance tests.

### 3.4.10 Cost Data

Costs are site-specific; however, an example of a system to process soil contaminated with ebonite battery cases, lead, arsenic, cadmium, and antimony was chosen to estimate costs. The estimate is based on the following:

- 10 MW furnace system;
- soil contaminated with approximately 20% casings and 3% lead;
- feed at maximum 30% moisture, dried to 3% or less in preparation;
- operation modes — 5-min oxidation cycle; 15-min oxidation cycle;
- operational (productive) time per year is 6,650 hr;
- total feed per cycle is 22 tonne (24 ton);
- carbon content per cycle — 15% of total feed in 20% casings;
- electrical cost per kWhr — \$0.04 (\$40.00/MWhr);
- labor, direct — 4 persons per crew, 4 crews @ \$16/hr;
- management not included;
- burden on labor — 60%;
- no credits taken for value of metals recovered;
- no credits taken for value of slag;
- no credits taken for the value of energy recovered;
- no credits taken for processing charges to customer;
- contractor finances capital costs; and
- miscellaneous electrical load by support equipment — 3 MW.

The basis for calculating operating costs is presented in Table 3.8 and is normalized to cost per ton in Table 3.9.

Capital costs are site dependent. They are also impacted by the amount of equipment leased compared with the equipment that must be purchased. The estimates of capital cost presented in Table 3.10 are for equipment only and do not include site, site preparation, security, site closure, or the cost of bringing electrical power or gas utilities to the site. The cost of functional buildings needed for the process are relatively minimal.

**Table 3.8**  
Annual Processing Rates and Power Requirements

Requirements	5 min Residence	15 min Residence
Tons of Feed Processed per year	87,192	80,000
MWHr (Electrical) per year	70,396	72,910

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**Table 3.9**  
Operating Cost per Ton of Material Processed

Operating Cost per Ton	5 min Residence (\$)	15 min Residence (\$)
Electrical	32.23	36.46
Labor, Direct	9.40	10.24
Labor, Indirect	3.45	3.76
Maintenance	7.35	8.00
Electrodes	3.10	3.30
Gases	2.10	2.25
TCLP	5.25	5.25
Refractories	3.45	3.75
Flux	2.10	2.25
Miscellaneous	2.30	2.50
<b>Total</b>	<b>\$70.80</b>	<b>\$77.76</b>

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Using the information in Table 3.10, leasing and depreciation costs can be estimated on the basis of cost per ton of material processed for a facility with a total capital cost of \$26,400,000 of which \$18,238,000 is for leased

**Table 3.10**  
Capital Cost Estimates

Item	Leased (Thousands of \$)	Not Leased (Thousands of \$)	Total
Buildings		2,200	2,200
Electrical 15.5 MW	1,500	500	2,000
Furnace 10 MW	8,300	2,200	10,500
Equipment Maintenance, Spares	550		550
Equipment, Mobile	210		210
Equipment, Wheel Wash	115	95	210
Furnace Ventilation	215	90	305
Personnel Facilities		300	300
Slag Casting	1,780	230	2,010
Bridge Crane	450	150	600
Engineering		635	635
Material Preparation	1,100	300	1,400
Material Feed System	600	175	775
Water Cooling System	590	220	810
Offgas System, Monitoring	1,170	325	1,495
Subtotal	16,580	7,420	24,000
10% Contingency	1,658	742	2,400
Total	18,238	8,162	26,400

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equipment, \$2,200,000 is for buildings, and \$5,962,000 is for equipment which must be purchased.

The annual cost for the major components either leased or amortized is:

Leased Equipment	\$18,238,000 @ 17.5%/yr for 8 yr = \$3,192,000/yr
Buildings	\$5,962,000 @ 7 yr = \$851,700/yr
Purchased Equipment	\$2,200,000 @ 10 yr = \$220,000/yr

The total capital cost of each major component is:

Leased Equipment	8 yr @ \$3,192,000/yr = \$25,533,000
Buildings	7 yr @ \$851,700/yr = \$5,962,000
Purchased Equipment	<u>10 yr @ \$ 220,000/yr = \$2,200,000</u>
Total Capital and Finance Costs	\$33,695,000

During the first seven years of operation, the capital cost totals \$4,263,000/yr. Therefore, the cost for 15 min residence time is \$53.29/ton (\$4,263,000 per 80,000 ton/yr) or for 5 min residence time it is \$48.90/ton (\$4,263,000 per 87,192 ton/yr).

A summary of the capital and operating costs normalized to one ton of material processed is presented in Table 3.11.

**Table 3.11**  
Summary of Total Operating and Capital Costs\*

Item	5 min Residence	15 min Residence
Total Capital Costs	\$26,400,000	\$26,400,000
Ton/yr at 6,650 hr/yr	87,192	80,000
MWhr of Electrical Power/yr	70,400	72,910
Electrical Demand Max. at 13.8 kV	15.5 MW	15.5 MW
Cost per ton of feed		
Operational	\$70.80	\$77.76
Financing	\$48.90	\$53.29
<b>Total</b>	<b>\$119.70</b>	<b>\$131.05</b>

\*Burden rate is 60% and no profit is included.

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### 3.4.11 Design Validation

Design validation procedures are usually based on acceptance tests that are best defined in the design specification package (see Section 3.4.9). It is also common practice to engage an independent peer reviewer during the procurement, design, and fabrication of the system to assess the information submitted.

### 3.4.12 Permitting Requirements

Regulatory compliance issues often drive remedial actions. The complexities of the Resource Conservation and Recovery Act (RCRA) and other regulatory requirements for conducting remedial actions at contaminated sites not only include the processes involved, but the need to identify regulatory constraints and cleanup goals in the early stages of a project to collect the appropriate data and provide the relevant remedy. Throughout the various phases of a project, the contractor should assist the regulatory agencies with the issues that affect a project, such as cleanup criteria, applicability of Land Disposal Restrictions (LDRs), and establishment of specifications to meet Applicable or Relevant and Appropriate Regulations (ARAR) or other regulatory requirements.

### 3.4.13 Performance Measures

Performance of a plasma furnace facility can be evaluated based on the degree of treatment and the amount of residual emissions of hazardous compounds. These measures are intended to protect human health and the environment during and after the treatment process.

Measures of the degree of treatment are:

- removal or reduced concentrations of toxic organics from contaminated soil; and
- removal or reduction of toxic metals from contaminated soil.

Measures of residual emissions of hazardous compounds are:

- trace organic waste constituents in the stack gas;
- products of incomplete reactions;
- acid gas emissions;

- toxic metal emissions;
- leachable toxic compounds from slag or metal residuals; and
- trace contaminants in control device fluids.

The techniques used to collect and analyze the samples that provide data on performance and emission levels are of critical importance. Essentially all feed streams and effluent streams must be sampled and then analyzed for a wide variety of constituents and physical or chemical properties.

#### **3.4.14 Design Checklist**

The key factors discussed in Section 3.4.2 (Design Basis) that a designer would need to consider when procuring and installing a plasma furnace are summarized in the following checklist.

##### **1. Design Basis Information**

- Feed system
- Flow rates
- Offgas composition
- Slag and metal
- Controls

##### **2. Utility Requirements**

- Auxiliary Fuel
- Electrical usage
- Process water
- Nitrogen/Oxygen
- Caustic

##### **3. Regulatory Requirements**

- Air permits
- Water permits
- Construction permits
- Operating permits
- Public involvement

#### **4. Site-Specific Considerations**

- Water discharge
- Meteorological conditions
- Seismic conditions
- Distance to nearest homes, businesses, schools





## IMPLEMENTATION AND OPERATION

### **4.1 Wet Air Oxidation**

#### **4.1.1 Implementation**

The principal supplier of Wet Air Oxidation (WAO) has been U.S. Filter-Zimpro (formerly Zimpro-Passavant Inc.). The company has designed and built most of the operating units, including construction of the major process vessels. It has provided preliminary test work on the actual materials to be oxidized, as well as start-up help plants after construction.

Some preliminary test work will be needed on any new material to set the operating conditions needed to meet the required product specifications. Temperature (with corresponding pressure) and residence time in the reactor are the variables that need to be defined in preliminary work. In general, the operating temperature is set for the most oxidation resistant component.

As pointed out previously, oxidation is never complete in WAO; some intermediate products remain. Preliminary work will define the analytical work needed to monitor the process; specific compounds will be chosen for monitoring the process to assure adequate reaction.

#### **4.1.2 Start-up Procedures**

Startup of a new WAO unit will have many of the same requirements of other chemical processes:

- operators must be trained, particularly in the use of the control program chosen;

- individual plant items need to be tested, e.g., air compressor, feed (water) pumps, control valves, heat-transfer equipment, etc.; and
- a surrogate may be tested before the actual feed, particularly if there is concern over the feed toxicity.

### 4.1.3 Operations Practices

Some scale formation can occur on heat transfer equipment and in the reactor. Commercial practice is to remove it periodically with an acid wash. Some pollution control equipment is usually required with WAO.

Liquid from the process will always contain incompletely oxidized material. In the usual case, the liquid will go to a biological wastewater treatment plant for complete detoxification of the effluent.

Offgas is usually suitable for direct exhaust to the atmosphere. In some cases, there is enough volatile organic in the gas or high enough CO content that further oxidation is needed. This may be either thermal (a small auxiliary burner) or catalytic.

### 4.1.4 Operations Monitoring

Temperatures, pressures, and flow are monitored. Reactor temperature and pressure must be kept within a pre-set operating window — too high a temperature suggests an unsafe condition that needs correction; too low a temperature will lead to inadequate conversion. Action must be taken, either to correct the situation or to shut down.

Offgas is monitored online for a number of constituents: oxygen, nitrogen, carbon dioxide, carbon monoxide, and total hydrocarbon. In addition, a constituent that is a characteristic partial oxidation product of the particular feed may also be monitored to ensure suitably complete oxidation.

The effluent is analyzed by laboratory procedures for typical wastewater parameters (COD, BOD, solids, ash, pH, TKN,  $\text{NH}_3$ , etc.).

The process area may be monitored for specific functional groups, depending on feed characteristics, particularly toxicity. Various analytical techniques have been applied for this purpose:

- Infrared
- Electron capture
- Conductivity
- Flame Ionization
- Flame Photometric
- GC

Personal monitoring and protective equipment must meet OSHA standards.

#### **4.1.5 Quality Assurance/Quality Control**

Quality assurance starts with the individual plant components and plant construction. Most components, such as compressors, pumps, valves, pipe and fittings, are standard and reliance is placed on the manufacturer. For special-purpose items, e.g., the reactor, suitable documentation and reference material, weld inspection, etc., must be provided.

Quality assurance in the complete plant is the responsibility of the construction contractor, with, presumably, oversight from the owner's engineer. Depending on the toxicity of the feedstock and other considerations, a detailed Quality Assurance plan may have to be provided to state or federal regulators. Responsibility for contact with regulators must be firmly fixed; compliance with environmental and safety requirements, keeping permits up-to-date, and maintaining contact with regulatory agencies, are essential elements of a Quality Assurance program.

A Quality Assurance plan for the plant operation after it has been turned over to the owner is mandatory, particularly so for toxic feeds. Records will have to be kept of effluents leaving the plant, and assurance will need to be given that effluents will be within agreed-upon limits.

## **4.2 Texaco Gasification Process**

Texaco normally provides design and licensing services for licensee owners, but is also open to the possibility of taking an equity position.

### **4.2.1 Implementation**

In a turnkey procurement, Texaco could bid the project on a turnkey basis and then subcontract the various components of the procurement.

### **4.2.2 Start-up Procedures**

Startup would be similar to the procedures followed in the chemical and oil refining industries where a start-up team from the major contractors is responsible for the initial tests and for working with the site operator to develop operations and maintenance manuals for the facility.

### **4.2.3 Operations Practices**

Operations would generally be carried out by the contractor responsible for the site remediation. This would generally include maintenance and calibration of the instruments, acquisition of measurements and samples for establishing the level of performance, and for reporting on unit throughput and performance.

### **4.2.4 Operations Monitoring**

The remediation contractor will monitor operations to ensure that requirements are met. In addition, the agencies responsible for the environmental effects of the cleanup would use the operations data and samples produced to determine that their requirements are met.

### **4.2.5 Quality Assurance/Quality Control**

The instruments used for monitoring water stream composition will require periodic validation by an independent laboratory.

## **4.3 Flameless Thermal Oxidation**

### **4.3.1 Implementation**

The method of implementation of Flameless Thermal Oxidation (FTO) for an SVE or GWS project depends on the needs of the

organization responsible for remediating the site. A private company would probably bid the project using the turnkey procurement process which includes all of the tasks necessary for successful remediation of the site. In a turnkey procurement, the PRPs responsible for the remediation would send a procurement specification to several architectural/engineering (A/E) firms. The procurement specification would define a scope of services to remediate the site with payment for the services to be a lump sum. The A/E firm selected would be responsible for the entire project. One of the tasks would be to develop a basis of design for the SVE or GWS offgas treatment as discussed in Section 3.3.2. This design basis would be incorporated into a procurement specification for FTO. The A/E firm would then work with Thermatrix on the detailed design, installation, startup, testing, and operation of the FTO.

A governmental organization, such as DOE or the Department of Defense (DoD), might choose to bid the project on a cost-plus fixed-fee basis. The DOE and DoD typically have large contractors operating their facilities or bases who would be asked to implement a remediation. The government contractor would then be responsible for developing the procurement specification and interfacing with Thermatrix and other equipment suppliers on the detailed design, installation, startup, testing, and operation of the system.

#### **4.3.2 Start-up Procedures**

After installation of the SVE or GWS equipment and the FTO equipment, the total system is ready for the start-up phase of the project. Startup typically includes the following tasks:

- operator and supervisor training;
- mechanical and electrical testing of the equipment;
- operation of the SVE or GWS with clean air or water while feeding the offgas into the FTO to ascertain if the FTO can achieve the design temperature at the design flowrate;
- preoperational testing on contaminated SVE or GWS offgas;
- performance testing (optional); and
- regulatory pretest and test program.

The preoperational testing optimizes system performance and establishes preliminary operating conditions that are used for the performance and

regulatory pre-testing and regulatory testing. The performance test can be used as a basis for acceptance of the final system. The regulatory testing can also be used as the basis for acceptance of the system. The regulatory pre-test is a practice test to make sure that the equipment can achieve the required test conditions and performance, and that the operators and the sampling and analytical contractors all understand what their responsibilities will be during the formal regulatory tests.

### 4.3.3 Operations Practices

A good design and a comprehensive operator training program are the best ways to assure satisfactory operation of the SVE or GWS and FTO. Most process upsets are handled by an automatic waste feed cutoff (AWFCO) system which is typically tied into a set of operational permitting conditions and initiated by a computer control system. Process upsets, such as low oxidizer temperature, instantaneously activate the AWFCO system and initiate corrective actions, such as higher levels of auxiliary fuel. The SVE or GWS computer control system also typically incorporates safety features into the design that also initiate AWFCOs or corrective actions to make sure the equipment and operators are protected and that the permit conditions are met.

Maintenance requirements for routine and non-routine maintenance are typically specified in one or more plans, such as a Health and Safety Plan, which are generally required by states and the US EPA for the remediation of contaminated sites. Except for routine maintenance, FTO is designed to operate with minimal operator attention.

### 4.3.4 Operations Monitoring

During operation of SVE or GWS with FTO, various process parameters must be monitored to ensure that the system is safely operated with minimal upsets and in compliance with the regulatory standards. Examples of regulatory and process parameters that might be monitored are:

- SVE or GWS offgas flowrate;
- SVE or GWS offgas temperature;
- negative pressure of the SVE system;

- the temperature of the FTO;
- wet scrubber process parameters, such as pH;
- the temperature in the stack;
- blower and pump on/off status; and
- fugitive emissions (usually by an equipment walk-through inspection).

#### 4.3.5 Quality Assurance/Quality Control

Quality Assurance/Quality Control (QA/QC) for SVE or GWS with FTO is generally handled by preparing a Quality Assurance Project Plan (QAPP) for the site. The QAPP presents the organization, objectives, functional activities, and specific QA and QC activities for the compliance testing and continuous emissions monitoring of the FTO. The QAPP also describes the specific protocols to be followed for sampling, sample handling and storage, chain-of-custody, and laboratory analyses during the test program. The contents of a typical QAPP include, but are not limited to, the following:

- project organization and responsibility;
- QA objectives (accuracy, precision, completeness);
- sampling procedures;
- sample custody;
- calibration procedures;
- analytical procedures;
- data reduction, validation, and reporting;
- internal quality control checks;
- performance and system audits;
- preventive maintenance;
- procedures for assessing data accuracy and precision;
- corrective action;
- QA reports; and
- analytical data packages.

## **4.4 Plasma Furnaces**

### **4.4.1 Implementation**

Preliminary assessments and site characterization are needed to develop a successful implementation plan. The preliminary assessment is often a quick analysis based on readily-available information, such as site management practices, information from generators, photographs, literature, and personal interviews. One goal of the preliminary assessment is to determine the urgency of the situation and to identify commercial, state, or federal parties ready, willing, and able to authorize the proper response.

Most frequently, companies that are responsible for site remediation ask for turnkey solutions for the project. In a turnkey solution, a single vendor will assume responsibility for all tasks necessary for a successful remediation and will prepare the overall project implementation plan. The overall plan encompasses detailed design, mobilization, startup, testing, and operating procedures for that particular system.

### **4.4.2 Start-up Procedures**

Several factors are essential for starting a remedial operation using a plasma furnace:

- development of Standard Operating Procedures (SOPs) and Limiting Conditions of Operations (LCOs);
- defining the Quality Assurance/Quality Control (QA/QC) measures;
- providing for safety concerns and emergency medical support;
- providing for laboratory testing and monitoring activities;
- defining, reporting, and process control protocols; and
- providing procedures for handling process upsets to ensure environmental compliance.

The contractor must demonstrate a thorough understanding of the overall process and how all the pieces fit together. A proactive approach to identifying potential problems is also desirable.



### 4.4.3 Operations Practices

A site remediation operator conducts daily activities that must be accomplished in strict accord with detailed SOPs and within exact operating parameters. Regulation requirements for the receipt, testing, treatment, transportation, and disposal of toxic and hazardous waste dictates strong controls for operational procedures and the use of control mechanisms to alarm and shut down systems before unsafe conditions occur. Operations personnel must review, update, and correct all SOPs and LCOs so they reflect current operating procedures and conditions at the remediation site.

All SOPs and LCOs should be thoroughly tested during pre-operational surveys to establish procedure/conditions validity, identify any potential problems, and verify personnel ability to execute. Testing should be performed with inert/simulated contaminated soil. The SOPs and LCOs should be used in the training program for site personnel. Those procedures and conditions specific to individual operations areas or tasks (e.g., lab analysis procedures, materials handling, control room operator responses to upsets, etc.) should also be used to *certify* that personnel know how to properly perform and respond *according to procedure*. The QA personnel should continuously ensure all operations adhere strictly to the SOPs and LCOs. The SOPs and LCOs need to be incorporated into checkoff lists for the shift Safety and QA/QC personnel to *verify* compliance.

### 4.4.4 Operations Monitoring

The remediation operator must provide accurate, continuous monitoring of the emissions and waste effluents for toxic or hazardous substances to ensure safe operation of the facility.

The operator needs to coordinate all matters related to environmental permits. Activities should be focused on keeping all permits up-to-date, monitoring/auditing to ensure compliance with all requirements, interacting with regulatory agencies via reports, and fulfilling all state and local regulatory requirements. The environmental monitoring program could include:

- establishment of background levels prior to operations;
- continuous review of permits;

## **Implementation and Operation**

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- permit modification and update;
- the establishment of an Audit Program;
- training of the workforce;
- hazardous waste management;
- monitoring for compliance;
- preparation of Environmental Compliance Plans;
- monitoring of trial performance tests;
- post sampling/monitoring; and
- closure certification.

### **4.4.5 Quality Assurance/Quality Control**

QA/QC encompasses and integrates the various tasks of a project (geotechnical, sampling, analytical, processing, and assessment) by requiring data to be representative, precise, and accurate within defined limits. Documentation, prepared and maintained according to the QA/QC plan, provides the defensible evidence of unbroken custody, traceability, and adherence to prescribed protocols and planned operations.

In addition, a Quality Assurance Project Plan (QAPP) specific to each project and each site should be prepared. Each QAPP is based on a QA/QC program. The QA/QC program and the QAPP define control activities, testing, and administration of the facility. The QAPP needs to include provisions for construction quality management and chemical quality management.

#### **4.4.5.1 Construction Quality Control**

A comprehensive Construction Quality Control Plan (CQCP) should be developed for all projects that involve excavation and removal of contaminated soil. This CQCP needs to be tailored to conform to the requirements of each site's scope of work. The plan encompasses the following main elements:

- construction quality assurance objectives;
- inspection activities;

- chemical quality control;
- corrective actions;
- documentation; and
- reporting.

Activities under the construction QA/QC plan include:

- perform preparatory, initial, periodic, and completion inspections for each segment of work, and maintain inspection records in a site file;
- maintain the project record documents;
- develop procedures, forms, and documents required to control procurement of equipment and materials required by the project;
- develop procedures, forms, and documents for the required submittal from all subcontractors;
- coordinate all activities with the Health and Safety Officer to ensure that the health and safety plan is being followed during all phases of work. Provide QA/QC oversight for the air monitoring program outlined in the Health and Safety Plan;
- ensure that construction of stormwater control structures are sufficient;
- implement VOC and dust controls, as necessary, during construction and remediation phases of the project; and
- during excavation and backfilling, activities will be scheduled and implemented to prevent cross-contamination of clean areas and to minimize the open cut areas.

QA/QC responsibilities include verification of areas for excavation, checking calculations of area and volumes for excavation, testing for possible VOC emission sources, validation or invalidation of verification sampling and testing, confirmation of suitability of backfill materials through sampling, development of control procedures for transport of contaminated materials, flood control procedures during excavation, and overseeing the placement, compaction, and contouring of backfill where applicable.

### 4.4.5.2 Chemical Quality Control

On-site fixation/stabilization projects typically involve testing of soils before and after treatment, groundwater/surface water testing, and some detailed record keeping.

Chemical quality assurance and control must be provided by the analytical testing laboratory tasked with the project. Any laboratory used should meet US EPA Contract Laboratory Program (CLP) requirements, as well as requirements or certifications of appropriate state regulatory agencies (e.g., the site/project state's environmental protection or health department). A specific Quality Assurance Plan for chemical parameters must be established that identifies:

- QA/QC objectives of the analytical laboratory;
- precision, accuracy, completeness, representativeness, and comparability of measurement data;
- sample holding times and turn-around times;
- a list of tests and the frequencies at which they will be performed;
- sampling procedures for each test;
- maintenance of a field log book;
- sample custody procedures and documentation;
- calibration procedures and schedules;
- analytical procedures;
- data reduction, validation, and reporting;
- internal quality control checks;
- performance and system audits;
- preventive maintenance procedures;
- corrective action for work which fails to meet QA/QC requirements; and
- quality assurance reports to management.

All field sampling, sample handling, and analysis must be performed in accordance with the QAPP and CQCP within the Construction Quality Management Program (CQMP), and all chemical analysis data will be examined according to US EPA Analytical Laboratory QA procedures to assure accuracy.



## CASE HISTORIES

### 5.1 *Wet Air Oxidation*

Detailed test work on a number of pesticides has been reported (Momont, Copa, and Randall 1995). The pesticides studied were:

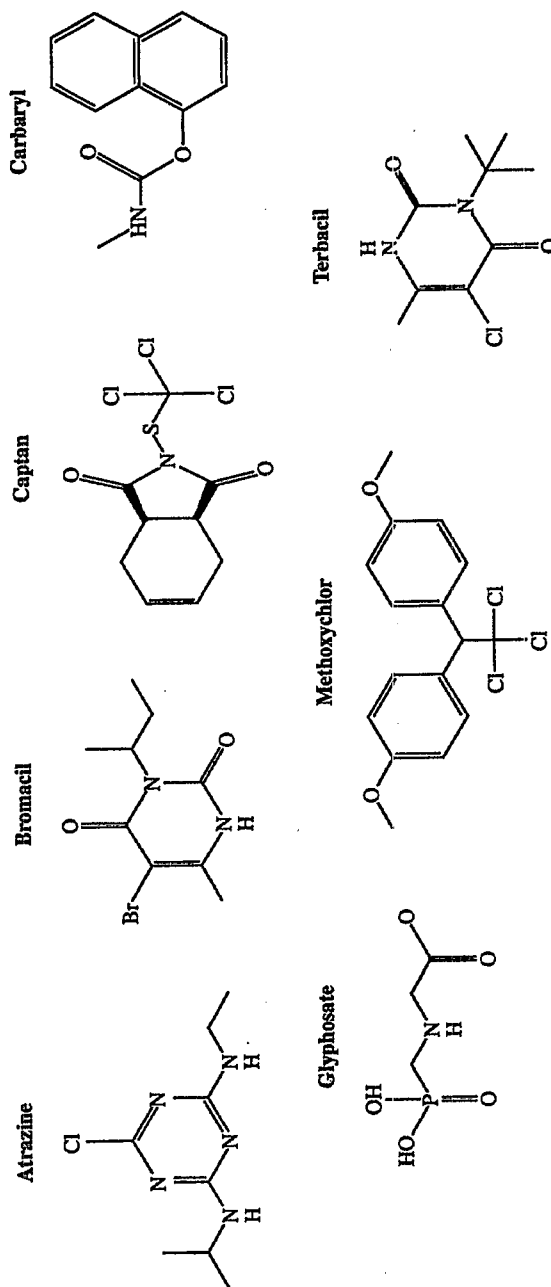
Fungicide:	Captan
Herbicides:	Atrazine
	Bromacil
	Glyphosate
	Terbacil
Insecticides:	Methoxychlor
	Carbaryl

Their structures are shown on Figure 5.1. Test work has also been done on other pesticides but with less-detailed reporting.

Complete test results reported for one of the pesticides, Glyphosate (commercial name — Roundup), are shown in Table 5.1. Similar detailed results have been reported for the other pesticides shown on Figure 5.1 (Momont, Copa, and Randall 1995). The data of Table 5.1 were obtained in a shaking autoclave, batch reactor.

The initial Glyphosate concentration was 14,600 mg/L, or 1.46%, a “typical” concentration for WAO operation. Extensive change of the carbon-phosphorus and carbon-nitrogen bonds occurred even at the lowest temperature conditions, 200°C (390°F); practically all of the phosphorus was converted to phosphate, and 99.5% of the Glyphosate was destroyed. However, large COD remained (52% of the original) representing organic

**Figure 5.1**  
Structures of the Pesticides Tested



Source: Momont, Copa, and Randall 1995

**Table 5.1**  
Characterization of Feed and Oxidation Products from the Oxidation of Glyphosate

Analyses	Autoclave Feed	200°C (390°F) for 60 min	240°C (460°F) for 60 min	280°C (540°F) for 60 min
COD, mg/L	27,500	14,400	9,300	6,900
COD Destruction, %	—	47.6	66.2	74.9
<sup>1</sup> NPOC, mg/L	7,500	5,800	3,900	2,300
pH	4.89	5.85	5.49	4.49
Total Solids, mg/L	24,000	15,500	10,800	10,000
Total Ash, mg/L	6,000	5,200	4,550	5,700
Total Kjeldahl Nitrogen, mg/L	2,320	2,440	2,190	1,320
Ammonia-N, mg/L	1,157	1,871	1,739	1,463
Nitrate-N, mg/L	<0.5	1	9	87
Total Phosphorous, mg/L	2,890	2,463	2,264	2,353
Ortho-P, mg/L	14	2,277	2,120	2,226
Glyphosate, mg/L	14,600	73	66	33
Glyphosate Destruction, %	—	99.5	99.5	99.8
<sup>2</sup> DIC, mg/L	< 10	800	300	< 1
Total Carbon in Offgas, mg/L	—	1,900	4,100	5,700
Total Nitrogen in Offgas, mg/L	—	< 200	870	850

<sup>1</sup>NPOC is Non-purgible Organic Carbon. (A sample is acidified and blown with air to remove material that is volatile at room temperature; the organic carbon on remaining material is measured.) In the past, this was frequently referred to as TOC: Total Organic Carbon.

<sup>2</sup>DIC is Dissolved Inorganic Carbon. This is carbon as CO<sub>2</sub> and carbonate. A sample is acidified and the CO<sub>2</sub> is measured.

Source: Momont, Copa, and Randall 1995

decomposition products remaining in solution. Higher conversions were obtained at 280°C (540°F) — over 75% of the organic carbon was converted to CO<sub>2</sub>; organic nitrogen was converted mainly to ammonia (over 60%) and nitrogen (36%).

Methoxychlor (a material with 31% chlorine by weight) was tested on a batch basis (shaking autoclave) and in a continuous flow unit. The feed concentration in the batch test was 4,400 mg/L. The feed to the continuous flow reactor was a process wastewater of much lower concentration, 8.84 mg/L. Destruction of 99.9% or higher was observed at a temperature of 275°C (527°F), with a 1-hour residence time in the batch reactor. The COD was reduced to 17% under these conditions. Essentially all of the chlorine in the original was converted to chloride ion in solution.

The continuous flow reactor produced results similar to that obtained by batch processing — over 99.9% destruction. The comparison is prejudiced somewhat by the extremely low concentration of methoxychlor in the feed. Oxygen mass transfer required from the gas phase was minimal as a consequence.

## 5.2 Texaco Gasification Process

A pilot-scale demonstration of the Texaco Gasification Process (TGP) was carried out at their Montebello, California facility as part of the US EPA SITE program. This facility had a nominal throughput of 23 tonne/day (25 ton/day) of coal (compared to 91 tonne/day [100 ton/day] for the proposed transportable facility). The material in this section was abstracted from the resulting SITE report (US EPA 1995).

The TGP produced a syngas suitable for feed for chemical synthesis facilities or for a clean fuel for the production of electrical power when combusted in a gas turbine. The average composition of the dry synthesis gas product consisted of 37% H<sub>2</sub>, 39% CO, and 21% CO<sub>2</sub>. No organic contaminants, other than methane (55 ppm), exceeded 0.1 ppm. The average heating value of the gas, a readily combustible fuel, was 239 Btu per dry standard ft<sup>3</sup>. The destruction and removal efficiency (DRE) for chlorobenzene, the designated principal organic hazardous constituent (POHC) exceeded the 99.99% remediation goal.



The average TCLP measurement for the coarse slag was lower than the regulatory levels for lead (5 mg/L) and barium (100 mg/L). The average California Waste Extraction Test-Soluble Threshold Limit Concentration (WET-STLC) measurement for the coarse slag was lower than regulatory value for barium (100 mg/L) and higher than the regulatory value for lead (5 mg/L).

Volatile heavy metals, such as lead, tend to partition and concentrate in the secondary TGP solid products — fine slag and clarifier solids. The average TCLP and WET-STLC measurements for these secondary TGP solid products were higher than the regulatory limits for lead, but lower than the regulatory limits for barium.

Texaco estimates an overall treatment cost of \$339/tonne (\$308/ton) of soil for a proposed transportable unit designed to process 90 tonne/day (100 ton/day) of soil with characteristics similar to that from the Purity Oil Sales Superfund Site, based on a value of \$3.30/1,000 kWhr (\$1.00/MM Btu) for the syngas product. Texaco estimates an overall treatment cost of \$248/tonne (\$225/ton) of soil for a proposed stationary unit designed to process at a central site, 180 tonne/day (200 ton/day) of soil with characteristics similar to that from the Purity Oil Sales Superfund Site, based on a value of \$6.60/1,000 kWhr (\$2.00/MM Btu) for the syngas product.

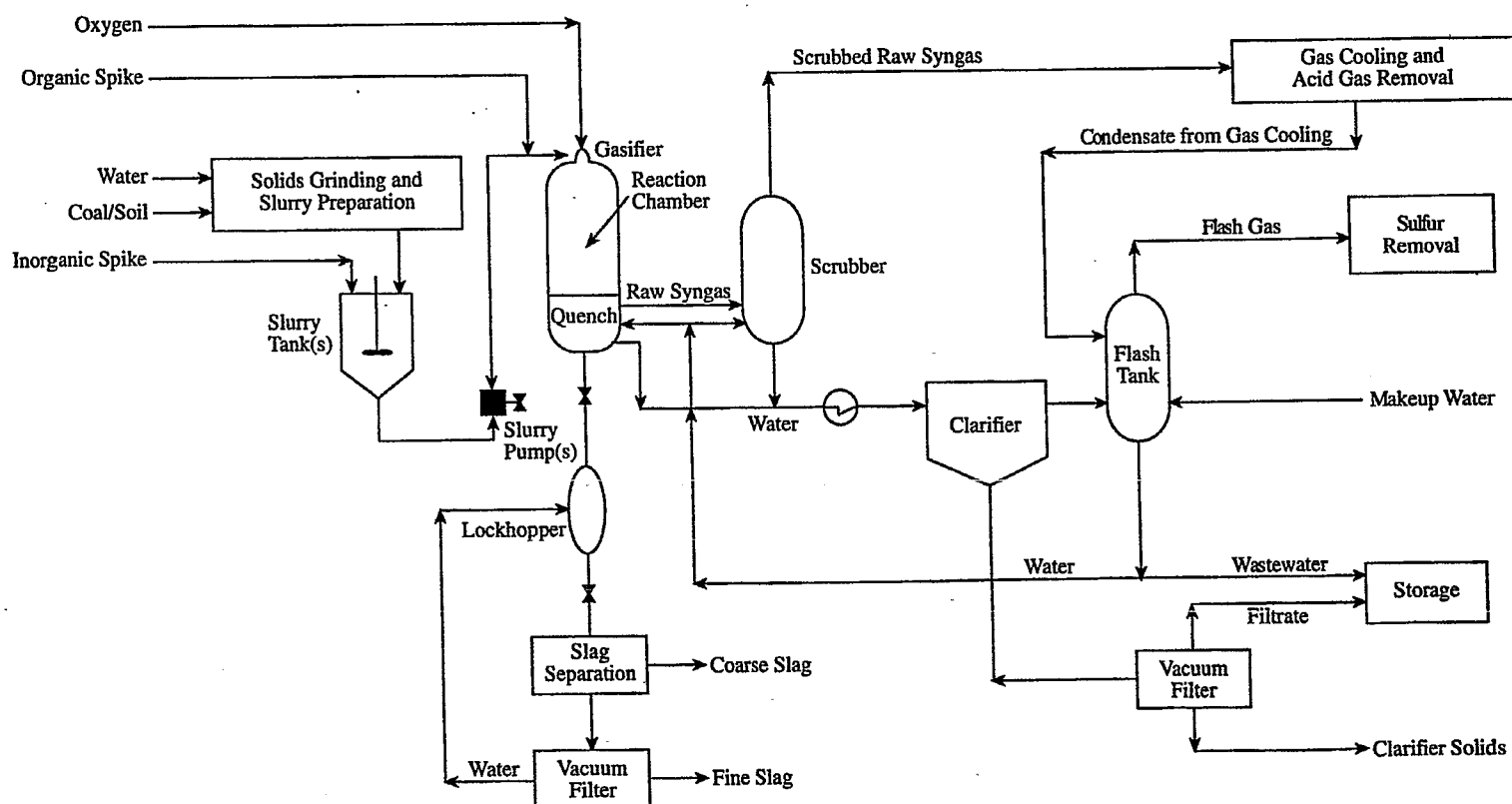
In continuous operations, proposed commercial units are expected to operate at on-stream availability of 70% to 80% to allow for scheduled maintenance and intermittent, unscheduled process interruptions.

The TGP technology evaluation applied the US EPA's standard nine criteria from the Superfund feasibility study process and the results are summarized in the following sections.

### 5.2.1 Equipment and Process Description

Texaco maintains three pilot-scale gasification units, ancillary units, and miscellaneous equipment at the Montebello Research Laboratory (MRL), where the SITE demonstration was conducted. Each gasification unit can process a nominal throughput of 23 tonne/day (25 ton/day) of coal. The SITE Demonstration used one of the three pilot-scale gasification units, the High Pressure Solids Gasification Unit II (HPSGU II), and support units as shown on the Figure 5.2 block-flow diagram. The diagram identifies the key MRL process units that are part of the overall facility.

**Figure 5.2**  
Schematic-Flow Diagram of the Texaco Gasification Process Used in the SITE Demonstration



### 5.2.1.1 Solids Grinding and Slurry Preparation Unit

The slurry feed used in the demonstration was a blend of the Purity Oil soil slurry and a clean soil slurry. Coal and clean soil were precrushed in a hammer mill. For each slurry, the precrushed product (coal and clean soil, site-screened Purity Oil waste soil and coal) was combined with water, an ash fluxing agent, and a slurry viscosity reducing agent in a rod mill, where the mixture was ground and slurried. The mill product was screened to remove oversized material and transferred to the HPSGU II slurry storage tanks where the inorganic spikes (lead and barium) were added.

### 5.2.1.2 High Pressure Solids Gasification Unit II

The slurry was gasified in MRL's HPSGU II. This unit includes equipment for slurry feeding, gasification, gas scrubbing, slag removal, clarifier solids removal, and process water handling. Figure 5.2 is a schematic-flow diagram of the process equipment and flows within the HPSGU II used in this demonstration. Figure 5.2 also defines the interaction of the HPSGU II process streams with other MRL TGP process streams and units.

During the demonstration, the slurry was spiked with chlorobenzene as it was pumped into the gasifier. The gasifier is a two-compartment vessel, consisting of an upper, refractory-lined reaction chamber and a lower quench chamber. Oxygen and slurry feeds were charged through an injector nozzle into the reaction chamber where they reacted under highly reducing conditions to produce raw syngas and molten slag. The oxygen-to-slurry ratio was controlled so as to maintain an operating temperature sufficient to convert the soil and coal ash into a molten slag. The average pressure was 3.5 MPa (500 psig).

From the reaction chamber, the raw syngas and molten slag flowed into the quench chamber, where water cooled and partially scrubbed the raw syngas. The raw syngas leaving the gasifier quench chamber was then further scrubbed of hydrogen chloride and particulates with additional water, cooled to near-ambient temperature, and routed to MRL's Acid Gas Removal Unit. More than 99% of the chlorides in the syngas were transferred to the circulating water in these steps.

The water quench transformed the molten ash into glass-like slag particles, which then passed down through the quench chamber/lockhopper system. The lockhopper system discharged the slag solids to a shaker

screen, which separated the slag into a coarse fraction (coarse slag) and a fine fraction (fine slag). The fine slag was recovered using a vacuum belt filter. The filtrate from the vacuum belt filter was recycled to the lockhopper system.

Water from the quenching and scrubbing steps was combined and cooled. Solids in the combined stream were removed using a clarifier, which produced an underflow stream of concentrated solids and water, called clarifier bottoms, and an overflow stream of clarified water. Periodically, the clarifier bottoms were drawn off and filtered to produce clarifier solids cake and filtrate. The clarifier effluent flowed to the flash tank where it combined with the condensate from the cooling of the raw syngas. In the flash tank, dissolved gases were removed from the water at low pressure (flash gas). Except for a small wastewater blowdown stream, the flash tank water was recycled to the gasifier quench chamber and raw gas scrubber.

The wastewater blowdown and clarifier bottoms filtrate were routed to temporary storage for testing prior to treatment and disposal.

### 5.2.1.3 Acid Gas Removal/Sulfur Removal

During the demonstration, MRL used a regenerable solvent process to separate hydrogen sulfide and carbonyl sulfide from the raw syngas. The raw syngas was contacted with the solvent, which removed the hydrogen sulfide, carbonyl sulfide, and some carbon dioxide (acid gases) producing a combustible fuel gas of low sulfur content. The fuel gas was then flared. The acid gases that were stripped from the solvent and combined with the gasification system flash gas were fed to the sulfur removal unit where the sulfides were absorbed by a caustic solution. The dissolved sulfides were oxidized with air and steam, producing a solution of sodium thiosulfate that was neutralized and routed to wastewater treatment. As with the fuel gas stream, the sulfur removal unit absorber and oxidizer offgas streams were flared.

### 5.2.2 Performance Data

To assess the TGP operation and its ability to process a RCRA-designated hazardous waste feed that does not comply with TCLP and WET-STLC regulatory limits, non-RCRA hazardous soil from the Purity Oil Sales Superfund Site in Fresno, California, was spiked with lead nitrate and

barium nitrate during slurry preparation to create a surrogate RCRA-hazardous waste feed. For the extended SITE demonstration, additional slurry was required and prepared using a mixture of clean soil and oil spiked with barium nitrate since further supplies of Purity Oil soil could not be obtained. To ensure a sufficient concentration of the designated Principle Organic Hazardous Constituent (POHC) for Destruction and Removal Efficiency (DRE) determination, chlorobenzene was added to the Purity Oil/clean soil mixed-test slurry at the slurry feed line to the gasifier. Table 5.2 shows the overall composition of the mixed, spiked-test slurry processed during the TGP SITE Demonstration.

Three runs were conducted over a 2-day period, treating approximately 36 tonne (40 ton) of slurry. The total amount of slurry treated during the entire demonstration (scoping runs, initial shakedown, system startup, a pretest run, the three replicate runs, and post-demonstration processing of the slurry

**Table 5.2**  
Composition of Demonstration Slurry Feed

	Purity of Soil	Slurry/lb	Total Mixed*
		Clean Soil	
Pittsburgh #8 Coal	10,511	56,280	66,791
Havoline SAE 30 Oil	—	2,050	2,050
L.A. County Soil	—	11,000	11,000
Fresno County Soil	—	11,080	11,080
Purity Oil Soil	5,264	—	5,264
Water	10,529	54,000	64,529
Gypsum	—	2,500	2,500
Surfactant	21	130	151
Barium Nitrate	330	1,000	1,330
Lead Nitrate	145	—	145
<b>Total</b>	<b>26,800</b>	<b>138,040</b>	<b>164,840</b>

\*The total slurry feed does not include the chlorobenzene organic spike (L-5) that was added (at approximately 3,150 mg/kg based on slurry flow) to the total mixed slurry flow to the gasifier at 6.20, 6.30 and 6.75 lb/hr for Runs 1, 2 and 3, respectively.

inventory) was approximately 90 tonne (100 ton). Critical process parameters included slurry feed rate; raw syngas, flash gas, and fuel gas flow rates; make-up and effluent water flow rates (except neutralized wastewater); weight of coarse slag, fine slag, and clarifier solids; and the organic spike flow rate. Critical chemical/analytical parameters included volatile organic compounds (VOCs), polychlorinated dibenzodioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), and metals in all feed and discharge streams (except neutralized wastewater); TCLP and WET-STLC analyses on waste feed, slurry feed, coarse slag, fine slag, and clarifier solids; and composition of process gas streams.

### 5.2.2.1 DRE

DRE is the measure of organic destruction. This parameter is determined by analyzing the concentration of the POHC in the feed slurry and the effluent gas stream(s). For a given POHC, DRE is defined:

$$DRE = \frac{W_{IN} - W_{OUT}}{W_{IN}} \cdot 100\% \quad (5.1)$$

where:  $W_{IN}$  = Mass feed rate of the POHC of interest in the waste stream feed; and

$W_{OUT}$  = Mass emission rate of the same POHC present in the effluent gas streams prior to release to the flare.

For these TGP SITE tests, DREs were calculated in two ways. For the gasification process, the effluent gas streams included the raw syngas and flash gas. For the overall TGP operation, the effluent gas streams included the fuel gas, the absorber offgas, and oxidizer offgas. The POHC identified for the demonstration was chlorobenzene. This compound was selected as a representative stable compound for the purpose of evaluating the TGP's ability to destroy organic compounds. As shown in Table 5.3, all calculated DREs were greater than 99.99% for chlorobenzene.

### 5.2.2.2 Slag and Solid Residuals Leachability

**Test Slurry Leaching Characteristics.** The test slurry was spiked with lead nitrate and barium nitrate to create a surrogate RCRA-hazardous waste feed and to evaluate the TGP's ability to produce a nonhazardous solid residual in which heavy metals are bound in an inert slag resulting in TCLP

**Table 5.3**  
Destruction and Removal Efficiencies (DREs) for Principal  
Organic Hazardous Constituent (POHC) — Chlorobenzene

DRE for Gasification Process					
Run	W* (lb/hr)	Raw Syngas (lb/hr)	Flash Gas (lb/hr)	Total W** (lb/hr)	DRE *** (%)
1	6.20	0.00016	0.000013	0.000173	99.9972
2	6.30	0.00019	0.000010	0.000200	99.9966
3	6.75	0.00023	0.000014	0.000244	99.9964
Average	6.42	0.00019	0.000012	0.000210	99.9967

DRE for Overall Texaco MRL Operation						
Run	W* (lb/hr)	Fuel Gas (lb/hr)	Abs. Offgas (lb/hr)	Oxid. Offgas (lb/hr)	Total W** (lb/hr)	DRE *** (%)
1	6.20	0.0000033	0.00010	< 0.000019	< 0.000122	> 99.9980
2	6.30	0.0000620	0.00038	0.000018	0.000460	99.9926
3	6.75	0.0000130	0.00023	0.000011	0.000254	99.9962
Average	6.42	0.0000250	0.00024	< 0.000016	< 0.000281	> 99.9956

\*W = Mass feed rate of chlorobenzene (POHC) in the waste stream feed.

\*\*W = Mass emission rate of chlorobenzene (POHC) in gas effluent streams.

\*\*\*DRE = The measure of organic destruction during the demonstration test. For a given POHC, DRE is defined  

$$DRE = [(W_{IN} - W_{OUT}) / W_{IN}] \cdot 100\%$$
 , where:  $W_{IN}$  = mass feed rate of the POHC of interest in the waste stream feed and  $W_{OUT}$  = mass emission rate of the same POHC present in the effluent gas streams prior to release to the flare.

and WET-STLC measurements that are lower than their respective regulatory limits. Table 5.4 shows that the test slurry feed measurements were higher than the TCLP and WET-STLC regulatory limits for lead, but lower than the regulatory limits for barium.

**Normalized TCLP and WET-STLC Values for Lead in Test Slurry.** The test soil composed of approximately 20% by weight Purity Oil soil (lead TCLP of Purity Oil soil: 223 mg/L) and 80% by weight clean soil (lead TCLP of clean soil: <0.03 mg/L) could be expected to have a normalized or corrected TCLP value for lead of approximately 40 mg/L. The test slurry composed of approximately 20% by weight total soil (normalized TCLP

## Case Histories

**Table 5.4**  
TCLP and WET-STLC Results — Lead and Barium

	TCLP Lead (mg/L)		WET-STLC Lead (mg/L)	
	Range	Average	Range	Average
Regulatory Value		5.0		5.0
Purity Oil Soil		223		—
Clean Soil (S-1)**		< 0.03		< 0.5
Slurry (SL-1)***	8.1-8.4	8.3	54-61	56
Coarse Slag (S-3)	3.3-5.8	4.5	6.7-11.1	9.8
Fine Slag (S-4)	11-18.3	14.9	22.8-52.9	43.0
Clarifier Solids (S-5)	691-1,330	953	903-1,490	1,167

	TCLP Barium (mg/L)		WET-STLC Barium (mg/L)	
	Range	Average	Range	Average
Regulatory Value		100		100
Purity Oil Soil		329		—
Clean Soil (S-1)**		0.3		< 5.0
Slurry (SL-1)***	0.1-0.2	0.1	< 5.0-5.5	< 5.5
Coarse Slag (S-3)	0.5-0.8	0.6	< 5.0	< 5.0
Fine Slag (S-4)	1.2-2.0	1.75	5.6-10.4	9.3
Clarifier Solids (S-5)	1.2-3.8	2.7	14-51.4	38.4

\*Lead TCLP of purity oil soil (waste feed to produce purity oil slurry) with 15,000 mg/kg (as elemental lead) lead nitrate spike and barium TCLP of purity oil solid with 30,000 mg/kg (as elemental barium) barium nitrate spike-measured in pretest spike study.

\*\*Clean soil is soil matrix used to produce clean soil slurry.

\*\*\*The SITE Demonstration slurry (SL-1) is a mixture of lead nitrate and barium nitrate-spiked slurries produced using purity oil soil and clean soil. SL-1 is composed of 26,800 lb of purity oil slurry mixed with 138,040 lb of clean soil slurry (See Table 5.2).

value for lead: 40 mg/L) diluted by the remaining slurry solution of 80% by weight coal, gypsum, and water (no lead TCLP value) could be expected to have a calculated TCLP value for lead of around 8 mg/L, which closely approximates the average TCLP measurement of 8.3 mg/L lead for the test slurry. Similarly, an expected normalized WET-STLC value of 280 mg/L lead, based on spiked soil blending, would be consistent with the average



WET-STLC measurement of 56 mg/L lead for the test slurry, due to the dilution of the coal, gypsum, and water.

***Fate of Barium in Test Slurry.*** The fate of the barium contaminant indicates that significant changes occurred in the barium chemistry during slurry formulation. A pretest TCLP value of 329 mg/L was measured in a leachate produced from the spiked Purity Oil soil. This contrasts with the much lower 0.1 mg/L measured in the TCLP leachate from the test slurry matrix, which included coal, gypsum, and water. The introduction of sulfur-containing gypsum and coal could have provided an environment in the slurry that changed the original soluble barium nitrate spike material to insoluble barium sulfate. The relative solubilities of barium nitrate and barium sulfate differ by ten-thousand fold. Since barium sulfate is relatively insoluble, it remains with the solids and does not transfer to the leachate during the TCLP test. The one thousand times reduction in the test slurry TCLP result for barium from the pretest level in the Purity Oil soil would be consistent with a partial speciation change to barium sulfate.

### 5.2.3 SITE Demonstration Results

The SITE demonstration showed that the mobility of the lead in the main residual solid product — the coarse slag — was lower than the mobility of the lead in the contaminated/spiked soil. The mobility of the barium essentially remained unchanged. The average TCLP and WET-STLC measurements for coarse slag, which comprised 62.5% by weight of the total solid residuals, were lower than the TCLP regulatory levels for lead and barium and the WET-STLC regulatory value for barium. The average TCLP and WET-STLC measurements for fine slag, which constituted 35.9% by weight of the total solid residuals, and clarifier solids, which amounted to 1.6% by weight, were higher than the TCLP and WET-STLC regulatory limits for lead but lower than the tests' regulatory limit for barium. The leach test results indicated mixed success in meeting the test objectives. Analysis of the effects of dilution by the non-contributing slurry components — coal, water, gypsum — on the TCLP and WET-STLC test results showed that the TGP can potentially produce a coarse slag product as its major solid residual with TCLP and WET-STLC measurements below regulatory limits. The TGP effectively treated a soil matrix exhibiting a normalized TCLP value of 40 mg/L lead and produced a coarse slag with an average TCLP value of 4.5 mg/L lead and a fine slag with an average TCLP value of 14.9 mg/L lead.

**Table 5.5**  
Comparison of the Composition of Raw and Treated Synthesis Gas

Raw Syngas Composition and Heating Value										
Run	H (vol%)	CO (vol%)	CO <sub>2</sub> (vol%)	CH <sub>4</sub> (ppmv)	N <sub>2</sub> (vol%)	Ar (vol%)	COS (ppmv)	H <sub>2</sub> S (ppmv)	THC (ppmv)	Heating Value (Btu/dscf)*
1	34.6	33.0	25.9	87	6.5	0.3	120	1,180	49	219
2	26.9	31.3	26.9	51	5.1	0.0	170	3,050	17	210
3	35.4	39.6	26.2	42	5.7	0.05	130	1,980	14	228
Average	32.3	34.6	26.3	60	5.8	0.1	140	2,070	27	219
Fuel Gas Composition and Heating Value										
Run	H (vol%)	CO (vol%)	CO <sub>2</sub> (vol%)	CH <sub>4</sub> (ppmv)	N <sub>2</sub> (vol%)	Ar (vol%)	COS (ppmv)	H <sub>2</sub> S (ppmv)	THC (ppmv)	Heating Value (Btu/dscf)*
1	37.6	39.1	21.0	71	5.8	0.2	33	490	32	239
2	38.3	35.0	20.9	49	4.9	0.05	44	580	16	239
3	34.7	41.3	21.2	44	5.6	0.1	50	68	15	239
Average	36.9	38.5	21.0	55	5.4	0.1	42	380	21	239

\*dry standard ft<sup>3</sup>

The average WET-STLC measurements for all solid residual streams were higher than the WET-STLC regulatory values for lead. However, the TGP demonstrated significant improvement in reducing lead mobility as measured by WET-STLC results. The process treated a soil matrix exhibiting a normalized WET-STLC value of 280 mg/L lead and produced a coarse slag with an average WET-STLC value of 9.8 mg/L lead and a fine slag with an average WET-STLC of 43 mg/L lead.

### 5.2.4 Synthesis Gas Product Composition

The syngas product from the TGP is composed primarily of hydrogen, carbon monoxide, and carbon dioxide. For a commercial unit, the raw syngas would need further treatment to remove hydrogen sulfide, typically, using an acid gas treatment system. This would produce a combustible fuel gas that could be burned directly in a gas-turbine/electrical-generation facility or could be synthesized into other chemicals.

The raw gas from the gasifier was sampled and analyzed to evaluate the TGP's ability to gasify a slurry containing a RCRA-hazardous waste material and produce a synthesis gas product. This gas stream was then treated in the MRL Acid Gas Removal System; the resulting fuel gas product was flared. Table 5.5 shows the composition of the raw syngas and the fuel gas products.

### 5.2.5 Products of Incomplete Reaction (PIRs)

The TGP is a gasification process which converts organic materials into syngas by reacting the feed with a limited amount of oxygen (partial oxidation). In addition to the syngas mixture of hydrogen and carbon monoxide, other organic compounds appear as products of the incomplete partial oxidation reaction. The term "PIR" describes the organic compounds detected in the gas product streams as a result of the incomplete reaction process.

All gas streams, including the raw gas, flash gas from the gasification section, fuel gas, absorber offgas, and oxidizer offgas, contained trace amounts of volatile and semivolatile PIRs. Carbon disulfide, benzene, toluene, naphthalene, naphthalene derivatives, and acenaphthene concentrations were measured in the gas streams at parts per billion (ppb) levels. The POHC, chlorobenzene, was also detected. Small amounts of methylene chloride and phthalates were also detected, but probably were sampling and

analytical contaminants. Measured concentrations of PCDDs and PCDFs in the gas streams were comparable to the blanks, indicating that these species, if present, were at concentrations less than or equal to the method detection limits (parts per quadrillion). Other compounds, such as xylenes, chloromethane, bromomethane, dibenzofuran, fluorene, and phenanthrene (expected from the thermal treatment of coal and chlorobenzene), were detected at lower concentrations in the flash gas and offgas.

### 5.2.6 Particulate Emissions

During the SITE demonstration, particulate emissions were measured for the raw syngas and fuel gas streams. These averaged  $6.1 \text{ mg/m}^3$  in the raw syngas and  $1.3 \text{ mg/m}^3$  in the fuel gas. By comparison, the particulate emission standards for boilers and industrial furnaces processing hazardous waste (40 CFR Part 266 Subpart H) and industrial, commercial, and institutional steam generators processing coal and other fuels (40 CFR Part 60 Subpart D(b)) are higher than the average measured values for these gas streams. Since the fuel gas product would not be vented or flared in a commercial unit, but would be burned directly in a gas-turbine/electrical-generation facility or synthesized into other chemicals, it is expected that the vent gas from any of these downstream facilities will be treated to meet applicable particulate emissions standards. This must be assessed on a case-by-case basis.

### 5.2.7 Acid Gas Removal

Measured hydrogen chloride gaseous emission rates ranged from 0.0046 to 0.0117 lb/hr. The chlorine concentration in the feed slurry, based on a chlorobenzene spike addition equivalent to 3,150 mg/kg in the slurry and the chloride concentration in the slurry, ranged from 4.3 to 4.7 lb/hr. Using these figures, the TGP's hydrogen chloride removal efficiency exceeded 99%.

Measured sulfur-containing gas emission rates ranged from 2.2 to 2.7 lb/hr. The sulfur concentration in the slurry, based on the ultimate analysis for sulfur, ranged from 0.97 to 1.20% by weight. Using these figures, the TGP's sulfur removal efficiency averaged 90%.

According to Texaco, the MRL systems for acid gas removal are designed to process a wide variation (flow and composition) of gas streams based on

the developmental nature of the research activities to which they are applied. It is expected that systems designed to meet the specific requirements of proposed commercial TGP units will provide higher removal efficiencies.

### 5.2.8 Metals Partitioning

The fate of the spike metals in the slurry (lead and barium) appeared to depend on their relative volatilities under TGP operating conditions. Lead — a volatile metal — concentrated in the clarifier solids, which were scrubbed from the raw syngas. Lead probably evaporated in the hot regions of the gasifier and condensed on the fine particles in the cooler areas of the process. The more refractory barium did not concentrate in any particular solid residue. It partitioned throughout the solid residual streams roughly in proportion to the mass of each residual stream.

The average lead concentrations were 880 mg/kg, 329 mg/kg, 491 mg/kg, and 55,000 mg/kg in the demonstration slurry, coarse slag, fine slag, and clarifier solids, respectively. Although the clarifier solids comprised only 1.6% by weight of the solid residuals, they contained 71.1% by weight of the measured lead in all the solid residuals. The remaining 28.9% by weight of the lead partitioned to the coarse and fine slags.

Average barium concentrations were 2,700 mg/kg, 11,500 mg/kg, 15,300 mg/kg, and 21,000 mg/kg in the demonstration slurry, coarse slag, fine slag, and clarified solids, respectively. The barium partitioned to the solid residual streams in approximate proportion to the mass flow of each stream. The coarse slag, which comprised 62.5% by weight of the solid residuals, contained 55% by weight of the measured barium in the solid residuals. The remaining 45% by weight of the barium partitioned to the fine slag and clarifier solids in approximate proportion to their mass flows.

### 5.2.9 Process Wastewater

The demonstration produced three process wastewater streams: process wastewater (flash tank blowdown and quench/scrubber and lockhopper water inventory on shutdown); gasification vacuum filtrate (produced from the vacuum filtration of the clarifier bottoms); and neutralized wastewater from the sulfur removal unit. Samples from each of these streams were collected and analyzed for VOCs, semivolatile organic compounds (SVOCs), PCDD/PCDF, metals, pH, and organic and inorganic halogens. Samples of the inlet

water stream were also analyzed to determine if the water supply was introducing any contaminants of concern.

Lead concentrations in the process wastewater and vacuum filtrate ranged from 12.4 to 38.9 mg/L and from 3.98 to 18.4 mg/L, respectively. Although the majority of the lead was found in the clarifier solids, small amounts of lead or lead compounds remained suspended in the clarifier effluent and traveled to the process wastewater as the flash tank blowdown. Similarly, small amounts of lead remained suspended in the vacuum filtrate and did not settle in the clarifier solids.

Trace concentrations of VOC and SVOC PIRs, such as benzene, acetone, carbon disulfide, methylene chloride, naphthalene and naphthalene derivatives, and fluorene were found in the wastewater streams. No concentrations of PCDDs or PCDFs were found at or above the method detection limit of 10 ng/L.

Inorganic chloride concentrations in the wastewater streams ranged from 380 mg/L to 6,800 mg/L. These values were, in general, an order of magnitude higher than the concentrations found in the inlet water; they indicated the presence of additional chlorides in the feed. Ammonia was also detected in the process wastewater and vacuum filtrate streams; the pH values of these streams were fairly neutral. The inorganic chloride concentrations indicated the presence of chloride, but the neutral pH values indicated that the chloride species is not acidic. These results show that the HCl produced in the gasification process was removed in the quench and scrubber, neutralized by the ammonia, and discharged in the process wastewater/vacuum filtrate effluents.

Concentrations of organic chloride in the inlet water, ranging from 680 mg/kg (Run 3) to 2,500 mg/kg (pretest), were carried through the system to the wastewater streams. Similar concentrations appeared in the process wastewater, vacuum filtrate, and neutralized wastewater streams.

For proposed commercial units, the wastewater streams would be treated on-site for recycling or for disposal as nonhazardous water.

### 5.2.10 Overall Unit Cost

Information available to date on capital and operating costs is preliminary. According to Texaco, an overall treatment cost of \$339/tonne (\$308/ton) of soil is estimated for a transportable unit designed to process 91 tonne/day

(100 ton/day) of soil with characteristics similar to that from the Purity Oil Sales Superfund Site, based on the production of a marketable syngas product valued at \$3.30/1,000 kWhr (\$1.00/MM Btu). Texaco estimates an overall treatment cost of \$248/tonne (\$225/ton) of soil for a stationary unit designed to process 180 tonne/day (200 ton/day) of soil at a central site, with characteristics similar to that from the Purity Oil Sales Superfund site, based on a value of \$6.60/1,000 kWhr (\$2.00/MM Btu) for the syngas product.

These costs include amortized capital costs and all operating costs. They exclude waste soil handling, waste site-specific roads and facilities, and permitting and regulatory costs, which can be extremely variable and are the obligation of the site owner or responsible party at the waste site. Actual costs will vary depending on the site and the soil matrix being treated.

### **5.2.11 Overall Unit Reliability**

The SITE demonstration experienced three operational incidents that were identified and resolved prior to startup or during operations; they did not require the shutdown and disruption of the demonstration operations. A major earthquake also occurred one day prior to the scheduled demonstration test. Based on the minimal disruptions caused by these incidents and the continuous post-demonstration processing of the remaining slurry inventory, the reliability and efficiency of the proposed commercial TGP units should be consistently high, and they are expected to operate at on-stream efficiencies of 70% to 80%. The downtime allows for scheduled maintenance and intermittent unscheduled shutdowns, such as those caused by materials-handling equipment problems due to variations in, and the abrasive nature of, soil and coal matrices.

## **5.3 Flameless Thermal Oxidation**

### **5.3.1 U.S. Department of Energy Savannah River Site SVE Demonstration Test**

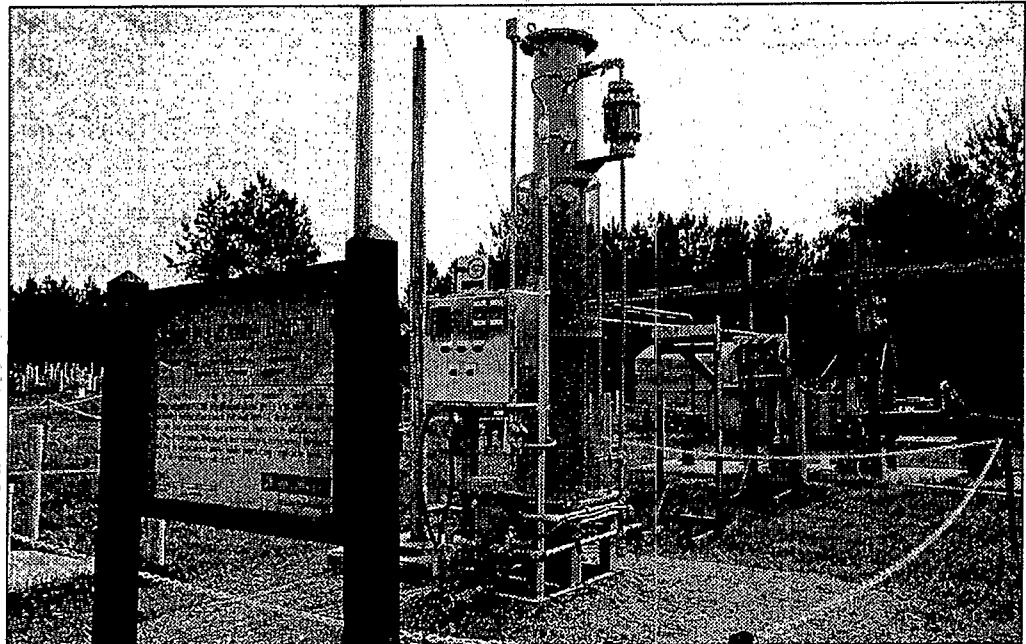
A demonstration test was conducted at the DOE Savannah River Integrated Demonstration site using FTO to treat the offgas from an SVE system (DOE 1995). The DOE's Savannah River Integrated Demonstration site is

## Case Histories

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located at the M-Area operations site where solvents were sent to an unlined basin with subsequent release to the groundwater beneath the basin. At the M-Area site, an 8.5 standard m<sup>3</sup>/hr (5 scfm) FTO unit was used to treat the offgas from an SVE system located within the one square mile VOC groundwater plume. The contaminants of concern at the site in the groundwater and the SVE offgas were 1,1,2-trichloroethylene (TCE), tetrachloroethylene (PCE), and 1,1,1-trichloroethane (TCA). A photograph of the FTO at the Savannah River Integrated Demonstration site is shown in Figure 5.3.

**Figure 5.3**  
DOE Westinghouse Savannah River Site, South Carolina



300 scfh from soil vapor extraction demonstration  
Chlorinated VOCs (TCE, PCE) - 99.999% DRE  
Installed early 1995

Reproduced courtesy of Thermatrix, Inc.



During the demonstration test, the FTO unit operated continuously at 870°C (1,600°F) for 22 days with an SVE flowrate of 8.5 standard m<sup>3</sup>/hr (5 scfm) and produced the following results:

- 11.17 kg (24.6 lb) of total chlorinated VOCs (CVOCs) were destroyed.
- The DE for PCE was >99.995%. No PCE was found above the detection limit during testing.
- The DE for TCE was >99.95%. No TCE was found above the detection limit during testing.
- The total CVOC DE was >99.95%.
- No products of incomplete oxidation were detected in FTO offgas during the continuous testing phase.
- Minimal operator attention was required; and no maintenance was required for the 22-day test period and for a total period of 6 weeks during the demonstration.

The DOE estimated that FTO would be more cost-effective than conventional thermal oxidation and catalytic oxidation (DOE 1995).

### 5.3.2 Full-Scale Treatment of Wastewater Stripper Offgas

While Thermatrix has not supplied any units for GWS offgas treatment, they have supplied an FTO to a chemical company for the treatment of the offgas from an air stripper handling 189 L/min (50 gal/min) of industrial wastewater. The FTO is a 170 standard m<sup>3</sup>/hr (100 scfm) unit followed by a wet scrubber because the oxidation offgas contains HCl. The FTO oxidizer is constructed of a corrosion-resistant, chromium-nickel-aluminum alloy (Binder, Martin, and Smythe 1994). Performance testing of the unit resulted in 99.97% to 99.99% DE for THC and 3 to 9 ppmv of CO on a dry gas basis, corrected to 7% oxygen.

## **5.4 Plasma Furnaces**

### **5.4.1 Brown's Battery Site Pilot-Scale Testing**

To evaluate the feasibility of using a plasma furnace to remediate soils from the Brown's Battery site, the Exide Corporation performed pilot tests using materials that would simulate the chemical and physical characteristics of the materials found at the site. Prior to completion of the pilot tests, substrate material was collected from a shale quarry containing soil of composition similar to that at the Brown's Battery site. Lead sulfate, fluxes, and ground battery case materials were added to the soil in proportions similar to those likely to be encountered during full-scale remediation of the site. The specific objectives of the pilot tests were:

- to prove the technology on a smaller scale than the proposed production-sized furnace for the Brown's Battery site using lead-contaminated soil and battery cases that were representative of the site;
- to test a DC transferred arc furnace equipped with a hollow electrode with the contaminated soil entering the furnace through the hollow electrode;
- to test the process under conditions (temperature, gas environments, and energy input) that would simulate the full-scale operational conditions; and
- to collect data on material and energy balances, material composition, and offgas properties.

The data from material and energy balances were used to validate process capabilities for lead removal and to provide information on the relative contribution of electrical energy and carbon combustion to furnace energy demands. The data from the testing of material composition and offgas properties were required for final engineering and permitting of the process.

Pilot testing was conducted in March, 1994, and June, 1994, at the Ontario Hydro Technologies (OHT) Lakeview Generating Station in Canada. Prior to the tests, a furnace and an offgas handling system were constructed using an existing power supply and scrubber. Mobile stack testing equipment was brought to the site for pilot tests. Samples of feed materials, slags, offgas dusts, scrubber solids, and other materials were collected during the

tests for analysis and calculating mass balances. Highlights of the test results follow:

- Lead removal rates for 1,118 kg (2,459 lb) of material processed in the furnace varied from 99.56% to 99.97%.
- Residual slags with total lead concentrations of less than 100 mg/kg were consistently produced under furnace operating conditions. Leachable lead concentrations, based on TCLP tests, were consistently below 0.6 mg/L.
- With proper attention to feed material processing, the electrode feed system can operate trouble-free.
- With the furnace operating under oxidizing conditions, the slag caused excessive deterioration of the furnace refractory and liquid iron heel. The rate of refractory attack was less pronounced when the furnace was operated under reducing conditions. A better refractory choice than castable MgO, taking into account the acidic nature of slag produced from the Brown's Battery site materials, should be considered for commercial operations.
- Under reducing conditions, iron oxides in the Brown's Battery site shale were reduced to iron metal and mixed with the iron heel for later recovery and use after separation from the slag.
- Offgas solids contained from 3% to more than 29% lead by weight — higher lead concentrations than offgas solids from commercial fuming operations. Higher lead concentrations in the offgas solids are desirable from the standpoint of reclamation of the solids.
- The calculated lead fuming capacity of the system greatly exceeded the furnace feed rate, suggesting that the process can treat materials with higher lead concentrations than those found at the Brown's Battery site.
- Slag from the process was tested and found to contain extremely low concentrations of antimony, arsenic, and cobalt, suggesting a potential for treating soils contaminated with these elements.
- With the final furnace design, air inlet rates ranged from approximately 85 to 170 m<sup>3</sup>/hr (50 to 100 ft<sup>3</sup>/min). Offgas flow rates ranged from 252 to 546 actual m<sup>3</sup>/hr (148 to 321 acfm) at

- temperatures ranging from 388 to 588°C (730 to 1,090°F). A commercial process would be able to better control these characteristics.
- Under oxidizing conditions, O<sub>2</sub> levels in the offgas were typically in the 12 to 13% by volume range. Under reducing conditions, in excess of 40% CO by volume could be attained in the offgas with less than 1% O<sub>2</sub> by volume. The reducing offgas also contained significant levels of H<sub>2</sub>.
  - The system exhibited a characteristic carbon consumption rate that could exceed the feed rate of carbon to the furnace and cause electrode consumption. This electrode consumption was suppressed at higher battery case feed rates.
  - Under strongly reducing conditions, oxygen was removed from the bath, indicating that the process can be used for smelting.
  - The offgas composition responded rapidly to the initiation and termination of heat. Response time from initiation of feed to constant offgas readings under reducing conditions was 4 min. At the termination of feed, the system required 6 min for O<sub>2</sub> levels to increase from 0.2% to 20.0% by volume (atmospheric).
  - Under reducing conditions, NO<sub>x</sub> levels in the offgas were typically below 10 ppm.

Overall, the pilot-scale test objectives were achieved. The testing validated the use of a DC transfer arc electric furnace for the specific waste tested.

### 5.4.2 Treatability-Scale Tests

In 1992, testing by the Exide Corporation included 5 batch tests using bench-scale test facilities; each batch contained 45 kg (100 lb) of soil, battery cases, lead, lead sulfate, and secondary lead smelter blast furnace waste. Thermal destruction was accomplished in a bench-scale, non-transfer arc plasma furnace. Slag characteristics (including residual metal concentrations and leachability) and lead removal rates were studied during these initial bench-scale tests. The results of the 1992 tests demonstrated:

- TCLP concentrations of 0.1 to 1.37 mg/L lead in the slag; and
- 99% or more of lead was removed from the waste materials.

Tests conducted in 1993 and 1994 used a TCLP test with lead detection levels of 0.1 mg/L lead. After HTMR published TCLP levels, Exide used a detection limit of 0.04 mg/L lead. Old samples were tested and found to have lead levels that were below the detection limit of 0.04 mg/L.

DATE	TIME	LOCATION	WIND	TEMP	SEA	REMARKS
1964	0800	1000	10	15	1	1000
1964	0900	1000	10	15	1	1000
1964	1000	1000	10	15	1	1000
1964	1100	1000	10	15	1	1000
1964	1200	1000	10	15	1	1000
1964	1300	1000	10	15	1	1000
1964	1400	1000	10	15	1	1000
1964	1500	1000	10	15	1	1000
1964	1600	1000	10	15	1	1000
1964	1700	1000	10	15	1	1000
1964	1800	1000	10	15	1	1000
1964	1900	1000	10	15	1	1000
1964	2000	1000	10	15	1	1000
1964	2100	1000	10	15	1	1000
1964	2200	1000	10	15	1	1000
1964	2300	1000	10	15	1	1000
1964	0000	1000	10	15	1	1000
1964	0100	1000	10	15	1	1000
1964	0200	1000	10	15	1	1000
1964	0300	1000	10	15	1	1000
1964	0400	1000	10	15	1	1000
1964	0500	1000	10	15	1	1000
1964	0600	1000	10	15	1	1000
1964	0700	1000	10	15	1	1000
1964	0800	1000	10	15	1	1000
1964	0900	1000	10	15	1	1000
1964	1000	1000	10	15	1	1000
1964	1100	1000	10	15	1	1000
1964	1200	1000	10	15	1	1000
1964	1300	1000	10	15	1	1000
1964	1400	1000	10	15	1	1000
1964	1500	1000	10	15	1	1000
1964	1600	1000	10	15	1	1000
1964	1700	1000	10	15	1	1000



## OTHER PROMISING TECHNOLOGIES

This Appendix provides information on ex-situ treatment processes under development that thermally destroy organics. They are presented in the context of thermal destruction technologies as defined in Section 1.1.

Appendix C provides a list of "Points of Contacts" for each technology discussed in this Appendix. The reader is encouraged to contact the listed persons or their organizations for the most current information.

For some technologies, as noted in the descriptions, metals are partitioned during the organic destruction process. This side effect of thermal destruction will, for the most part, facilitate subsequent metal recycle or stabilization for disposal.

All technologies must be considered as part of a total treatment system if they are to be compared for a particular application. Such a system must account for (a) all treatment functions, not just thermal destruction, (b) technology interfaces within the system, (c) material balances within the system, and (d) the different waste types (liquids, sludges, debris, etc.) and hazardous contaminants that are to be treated.

### ***Organic Destruction Using Solar Energy***

Solar technology has been proposed for the destruction of toxic organics (Schwinkendorf et al. 1995). Applications to date are directed at the destruction of gaseous or liquified organic contaminants that are thermally desorbed from contaminated soils. Solar technology is also applicable to liquid, semi-volatile and volatile wastes generated by other processes. Solar destruction technologies often rely on both conventional and solar radiation destruction to maximize organic destruction efficiencies. In some cases, solar destruction occurs in a separate stage where the remaining high

molecular weight products of incomplete combustion from the conventional stage (e.g., dioxins, furans and PCBs) are destroyed. Concentrated solar fluxes between  $100 \text{ W/cm}^2$  ( $645 \text{ W/in.}^2$ ) and  $230 \text{ W/cm}^2$  ( $1,484 \text{ W/in.}^2$ ) are used to destroy organic contaminants (Glatzmaier et al. 1990; Ball et al. 1992). Organic destruction efficiencies are between 99% and 99.999%, depending on the organic contaminant, the type of solar reactor, and the reactor operating conditions.

The DOE, through its National Renewable Energy Laboratory (NREL) in Golden, Colorado, has been studying solar destruction since 1986. Laboratory and field testing has shown that photons in the ultraviolet portion of the solar spectrum significantly decrease the products of incomplete combustion in the offgas. For fiscal years 1990 through 1992, the US EPA budget included a line item for cooperative work with DOE in investigating the use of this technology to treat various kinds of waste. In fiscal year 1991, the DoD budget included a line item providing \$5 million to research, develop, test, and evaluate a fully functional solar unit. In 1991, a tri-agency agreement (involving US EPA, DOE and DoD) was formed to develop solar technology for destruction of hazardous organic wastes. Solar organic destruction technology is still in the test and evaluation phase and has not yet been commercialized. Nonetheless, this technology is being considered for soil decontamination applications at various military sites.

Two specific systems were developed through the tri-agency agreement, one by Midwest Research Institute (MRI), Kansas City, Missouri, and the other by Science Applications International Corporation (SAIC), Golden, Colorado.

US EPA and DOE have sponsored the evaluation of the two-stage solar destruction technology by MRI through the US EPA National Risk Management Research Laboratory (NRMRL), Cincinnati, Ohio. Liquid and semi-volatile organics, or thermally-desorbed volatilized organics are injected into the first stage, mixed with air, and combusted. Combustion products are then transferred, at temperatures up to  $960^\circ\text{C}$  ( $1,760^\circ\text{F}$ ) into the second stage where solar radiation is used to destroy residual Principle Organic Hazardous Constituents (POHCs) and Products of Incomplete Combustion (PIC) in the combustion products. Based on fundamental studies and tests conducted at the DOE High-Flux Solar Furnace (HFSF) at NRMRL, MRI has developed and tested the Minipilot Solar System (MSS) for thermal treatment of liquid organic waste and solar destruction of



combustion products. After a nonsolar operational performance demonstration, the MSS underwent full solar testing (up to 8 kW solar power) at the HFSF at NRMRL. Typical MSS full solar operating temperatures were in the range of 818 to 826°C (1,504 to 1,519°F). At these conditions, it was found that organic destruction was high, 99.999% or greater, but that solar irradiation did not provide significant emissions reductions relative to non-solar operations. On the other hand, irradiation with artificial ultraviolet light did reduce the emission of volatile PICs. The NRMRL solar demonstration provided unexpected yet critical data needed for future study of emissions phenomena and design information for a larger pilot or full-scale systems (US EPA 1994b; Gorman et al. 1996).

SAIC has completed the design phase of a DoD, U.S. Army Environmental Center (AEC), contract for demonstration of a full-scale system (U.S. Army Environmental Center 1993) installation of a solar demonstration facility at the Sierra Army Depot in Herlong, California (Glatzmaier et al. 1993). Energy and Environmental Research Corporation (EERC) and International Technologies (IT) are supporting SAIC in the integral combustion/solar destruction reactor and soil vapor extraction system designs, respectively. The SAIC solar system features a faceted, stretched-membrane dish solar concentrator and an integrated, single-stage, high-temperature combustion and solar detoxification reactor. Operating temperatures within the reactor are approximately 1,000°C (1,800°F) and residence times are 1 to 2 sec. Simulated soil vapors will be condensed and transferred to the reactor as liquid waste at flow rates up to 12.3 kg/hr (27.3 lb/hr). Offgases are treated and scrubbed before they are released. The effort will culminate in the full-scale demonstration, scheduled to begin in late 1996 (Davenport et al. 1995).

## ***Thermal Catalytic Oxidation***

Thermal Catalytic Oxidation (TCO) is used to destroy VOCs and CVOCs in moderately contaminated gaseous waste streams (DOE 1995a). Original catalysts for destruction of CVOCs were subject to irreversible chlorine poisoning of the active metals. However, new catalysts developed in the early 1990's are much more resilient to metal chloride formation and TCO has emerged today as a reliable baseline treatment method.

Current applications of TCO employ monolith catalyst blocks constructed of a ceramic base with a wash coat of metal or metal oxide impregnated alumina. TCO systems can be designed to handle flow rates from 0.3 to 300 m<sup>3</sup>/min (10 to 10,000 scfm), and as such, are applicable for typical soil vapor extraction and air stripping offgas treatment operations. Operating temperatures range from 250 to 600°C (480 to 1,100°F). At these temperatures, energy needs, electrical or natural gas, range from 15 to 20 kW, per each 2.8 m<sup>3</sup>/min (100 scfm) of humid air flow. This energy is about half that required for incineration. TCO systems require caustic scrubbers for CVOC operations. TCO is subject to fouling, active metal poisoning, and metal particle sintering, as are all catalytic operations. As a result, catalyst replacement times are on the order of three years.

Several different catalysts have been tested and used in offgas treatment operations at DOE's Savannah River Site in South Carolina. An early 0.3 m<sup>3</sup>/min (10 scfm) pilot-scale test using a Johnson Matthey monolith catalyst was conducted in 1992. This test was conducted as part of the DOE's Office of Technology Development, VOCs in Non-Arid Soil and Groundwater Integrated Demonstration. Results show that organic destruction efficiencies equal to or greater than 99% could be achieved at temperatures above 500°C (930°F) for each compound in a waste stream containing perchloroethylene (PCE), trichloroethylene (TCE), and 1,1,1-trichloroethane (TCA) (Jarosch et al. 1994).

Current full-scale soil vapor extraction units, 6 to 23 m<sup>3</sup>/min (200 to 800 scfm), are in operation. These units use either a newer, lower operating temperature Johnson Matthey catalyst that is less susceptible to poisoning, or an Allied Signal catalyst. Both catalysts operate at temperatures ranging from 400 to 450°C (750 to 840°F) and can achieve organic destruction efficiencies greater than 98% for a broad range of toxic organics.

## ***Fluidized Bed Cyclonic Agglomerating Combustor (AGGCOM)***

AGGCOM is a two-stage organic destruction and ash agglomeration (vitrification) process for remediating soils and sludges contaminated with both organic and inorganic compounds. AGGCOM combines two environmental

remediation technologies developed by the Institute of Gas Technology (IGT)(US EPA 1991; Mensinger et al. 1991). The first stage is based on a sloping grid, fluidized-bed (SGFB) technology originally developed for coal gasification applications. Both organic destruction and ash agglomeration are accomplished in the SGFB stage. The bulk of the fluidized bed operates at temperatures between 820°C (1,500°F) and 1,100°C (2,000°F). The central spout in the bed operates at a sufficiently higher temperature to partially fuse and agglomerate the ash and immobilize inorganic contaminants, such as metals, in the glassy, agglomerated ash matrix. Additional destruction of gaseous organics and products of incomplete combustion leaving the first stage is achieved in a high intensity, second stage, cyclonic combustor where inorganic fusing and agglomeration is completed. Overall organic destruction efficiencies range up to 99.99%.

The two-stage AGGCOM process has been under development at IGT for several years. Bench-scale [15 cm (6 in.) diameter, 9 kg/hr (20 lb/hr)] SGFB test results were used to establish operating conditions for acceptable soil agglomeration in the pilot-scale AGGCOM unit. Leaching characteristics of the soil agglomerates were determined. A 0.9 m (3 ft) diameter SGFB unit was tested with coal (over 10,000 hr of operation) and demonstrated that agglomerated ash can be readily produced. Agglomerated ash samples passed the Extraction Procedure (EP) Toxicity Test.

The bench-scale unit was also tested with spent blast abrasive and spent foundry sand at feed rates between 450 kg/hr (1,000 lb/hr) and 900 kg/hr (2,000 lb/hr). Both wastes were contaminated with 1% to 2% organics. In the spent blast abrasive tests, it was determined that organic destruction exceeded 99.99% for the tributyl tin oxide contaminant, and the reclaimed blast abrasive was suitable for reuse under U.S. Navy specifications. The spent foundry sand test yielded similar results.

In separate testing, the cyclonic combustor has been evaluated in a 0.84 GJ/hr (0.8 MM Btu/hr) unit at a feed rate of 14 kg/hr (30 lb/hr) to 27 kg/hr (60 lb/hr) of surrogate wastes. Carbon tetrachloride ( $\text{CCl}_4$ ) destruction efficiencies exceeding 99.9999% were achieved under less than optimum conditions (Rehmat et al. 1995).

More recently, a series of soil agglomeration tests was conducted with raw and spiked samples of soil in the bench-scale unit. Agglomerated or vitrified soil samples were produced in four of eight tests that were conducted. Operating conditions to achieve soil agglomeration were confirmed,

samples passed the Toxicity Characteristic Leaching Procedure (TCLP) tests, and results indicate that higher contaminant levels can be processed by the AGGCOM process.

This technology was accepted into the Superfund Innovative Technology Evaluation (SITE) Emerging Technologies Program in July, 1990. A 5.4 tonne/day (6 ton/day) two-stage, pilot plant has been constructed and tested, producing additional agglomerated soil samples under various operating conditions (Mensinger et al. 1991). Future testing of the AGGCOM process will focus on the sustained and continuous operation of the pilot plant with soil admixed with both organic and inorganic surrogate compounds. Plans are to test other feedstocks, such as industrial waste, auto shredder fluff, and medical wastes.

### ***Hybrid Fluidized Bed System***

The Hybrid Fluidized Bed System is a three-stage system designed to treat soils and sludges contaminated with toxic organics and volatile inorganics (US EPA 1991). The first stage consists of a spouted bed that operates at an inlet velocity of 46 m/sec (150 ft/sec) and a temperature between 820°C (1,500°F) and 930°C (1,700°F). Large particles are retained in this stage until they are reduced in size through abrasion and grinding. System advantages based on calculations and limited experimental work include better heat transfer for large clumps of dirt as compared to conventional rotary kilns, and less pressure drop as compared to a conventional fluidized bed. Fine particles, volatile metals, and organic compounds pass to the second stage, the fluidized bed afterburner, where the organic compounds are further destroyed. Upon testing, materials that absorb metal vapors (i.e., silica sand, alumina balls, and steel shot), capture fine particles and promote the formation of less mobile metal compounds. Processed soil is removed in the third, hot cyclone stage. Offgases are quenched and treated in a conventional baghouse for particulate and metal control. Organic destruction efficiencies range up to 99.9% and metal removal efficiencies range up to 95%.

Bench-scale tests were conducted in 1989 to determine the ability of the fluidized bed materials to capture metals (Energy and Environmental Research Corporation 1992). Capture rates for volatile metals of 85% to

95% were achieved. A 30 cm (12 in.) diameter pilot-scale unit was constructed and tested in 1991 under a Small Business Innovative Research (SBIR) grant. This system was operated in a short-term batch mode at a feed of 2.3 kg/5 min (1 lb/min), with a soil feed spiked with organics and metals. Greater than 99.9% removal of contaminants was achieved.

This technology was accepted into the SITE Emerging Technologies Program in July, 1990. A Process Development Unit (61 cm diameter, continuous feed at 227 kg/hr [24 in. diameter, continuous feed at 500 lb/hr]) was built and mechanically tested with soil feed (Mensing et al. 1994). The system was then modified to convert the spouted bed from an oxidation to a gasification system and to add an afterburner after the fabric filter. It was then tested with an auto shredder residue feed. A modified pilot-scale unit with a processing capacity between 450 kg/hr (1,000 lb/hr) and 680 kg/hr (1,500 lb/hr) has been constructed and operated (US EPA 1993).

## ***Metallurgical-Based Treatment Processes***

Metallurgical-based treatment processes employ a molten metallurgical bath to destroy organics, capture inorganic contaminants, such as metals in the bath, and produce a leach-resistant waste form (Schwinkendorf et. al. 1995). The processes accept a wide variety of waste after size reduction. Waste is introduced into the molten bath, e.g., iron or an alumina matrix, within a refractory-lined vessel. Methods of forming the molten bath include electrical induction coil and combustion heating. In the bath, waste constituents separate into metallic and oxide slag layers, and offgas products. Separation of metals from the slag depends on properties of the constituents, process additives, and the operating environment. The metals and slag can be recovered from the melt. The metals can either be recovered and recycled, or stabilized for disposal. The oxide slag, after any required stabilization, is usually disposed. Offgases can be treated to recover or recycle reusable constituents or processed through an air pollution control system before being released. Toxic organics are destroyed in the intense heat of the bath, up to 1,800°C (3,300°F), at destruction efficiencies exceeding 99.9999% for some organics.

Metal melting and refining technology is an established decontamination method in which contaminated steel, copper, or other contaminated wastes are melted within a molten bath. Generally, these processes have been adapted to treat hazardous wastes and can be applied in some cases to treat mixed radioactive and hazardous wastes. Research and development requirements continue to be addressed including (a) pretreatment system demonstrations, (b) bulk solid feed methods, (c) component operability, performance and lifetime, (d) DOE mixed waste treatment demonstrations, (e) heating methods for high nonmetal waste feeds, and (f) organic content effects on radionuclide partitioning and particulate generation.

Ausmelt, Ashland, and M4 Environmental L.P. (M4) are actively promoting metallurgical-based technologies for waste treatment applications.

Ausmelt Technology Corporation of Denver, Colorado, has demonstrated its system, including the use of a patented lance that is submerged in the molten metal (Lightfoot et al. 1992). A total of 10 Ausmelt facilities are now in operation. A 90,000 tonne/yr (99,000 ton/yr) facility to process lead slag started operation in 1992 and a 120,000 tonne/yr (132,000 ton/yr) plant to treat zinc leach residues is under construction, both in South Korea. Data on processing a variety of wastes, approximately 30 different materials, have been generated in pilot plants in Australia, France, and Colorado. Each pilot plant has a capacity of 200 kg/hr (440 lb/hr).

Ashland Petroleum's Hymelt® (Ashland 1995) is another metallurgical process that has been operating for over a year at the pilot-plant stage. The reactor has two chambers, one yields hydrogen and the other yields carbon oxides. Demonstrated waste feeds include trash, garbage, bacteriological hazardous waste, chemical agents, and other, principally high hydrocarbon, wastes.

M4, a Molten Metals Technology (MMT) and Lockheed Martin Corporation partnership, was established in 1994 to demonstrate and apply the Catalytic Extraction Process (CEP) to waste streams at DoD, DOE, and other government and private facilities. MMT developed CEP under DOE sponsorship (Sheridan 1993). A related technology, Quantum CEP™, has been developed for processing radioactive and mixed radioactive and hazardous wastes. CEP uses an inductively-heated molten metal bath. Potentially marketable metals can be recycled. CEP destruction efficiencies are reported to exceed 99.9999% for dioxins, furans, and other hazardous organics, including chemical warfare agents. CEP was recently designated by US

EPA as the Best Demonstrated Available Technology (BDAT) for all waste for which incineration had been the only approved processing method. Additionally, several states have approved CEP as a recycling technology, confirming it to be distinct from incineration.

A multiple unit Quantum-CEP™ facility is operating at M4's Technology Center in Oak Ridge, Tennessee. The center is being used for research and development, and full-scale processing of mixed waste from government, commercial, and university sources (M4 Environmental L.P. 1996).

## ***Molten Salt Oxidation***

Molten Salt Oxidation (MSO) is a flameless, high temperature molten salt pool process that (a) destroys toxic organics, (b) separates and retains toxic metals, radionuclides, and products of incomplete combustion in the molten salt residue, and (c) treats acidic gas by-products (Adamson et al. 1995; Schwinkendorf et al. 1995). MSO operating temperatures are between 700°C (1,300°F) and 950°C (1,740°F), temperatures at which salt viscosity is similar to that of water. External electric or natural gas heaters are used to heat the salt to operating temperature and in most cases the pool is kept at these temperatures by the heat of oxidation of the organics. The salt is generally sodium carbonate or an eutectic of alkali carbonates. Test results indicate that Inconel 600 is an acceptable material for the pool vessel. Results also indicate that the vessel may require a ceramic liner for some applications.

Candidate waste streams for MSO treatment are high heating-value materials, such as spent solvents, oils, and other organic liquids; crucible graphite; plutonium-contaminated leaded gloves; ion exchange resins; granulated solids; and energetic materials such as explosives, propellants, and pyrotechnics. Both waste and oxidant air are injected into the bottom of the molten salt pool. Organic destruction efficiencies have exceeded 99.9999% in some cases. Metal and radionuclide molten pool retention fractions are 99% or better, depending on the metal/radionuclide and operating conditions (Gay 1991; Stelman et al. 1992). Tests indicate that potential offgas emissions can be maintained at relatively low levels, but a suitable offgas system may be required for some applications (Watkins et al. 1994).

MSO advantages include catalytic acceleration of oxidation rates, enhanced organic destruction efficiencies due to high mass and heat transfer rates within the liquid salt, resistance to thermal surges, and stability with respect to variations in waste feed. Disadvantages include limitations on types of treatable wastes, the potential of molten salt freeze-up in process equipment, and added requirements for molten salt recycle. The latter provides for continuous-mode operations and the removal of entrapped metals and radionuclides to avoid performance degradations.

MSO was developed by Rockwell International and the U.S. Navy in the 1970's for disposal of explosives and propellants (Darnell et al. 1974) and later for coal gasification and the processing of radioactive waste (Cudahy et al. 1993). Waste treatment applications were recognized and laboratory-scale, bench-scale and pilot-scale MSO units were operated at the Energy Technology Evaluation Center, Rockwell International, and Lawrence Livermore National Laboratory (LLNL), all in California, and Oak Ridge National Laboratory in Tennessee (DOE 1993). A DOE peer review (Cudahy et al. 1993) identified a number of unresolved MSO issues, e.g., the pretreatment of solids, materials of construction, melt freeze-up, monitoring of residues in the melt, and molten salt recycle. MSO test units continue to be operated to address these and other development issues. An example of an operating MSO unit is the LLNL 2 kg/hr Engineering Development Unit. This unit is currently being operated to resolve engineering design and development issues.

LLNL, the Naval Surface Warfare Center (NSWC), other government laboratories, and MSO equipment suppliers are now cooperating in a combined effort to bring laboratory and commercial expertise together to resolve MSO design implementation issues. Current efforts are focused on design and development of a 5 kg/hr (11 lb/hr) pilot-scale unit for planned implementation at LLNL (Hersey 1994) and a pilot-scale unit for implementation at NSWC.

## **Steam Reforming**

Steam reforming is a mature industrial process that is used to make hydrogen gas from methane (Schwinkendorf et al. 1995). This process is being applied to treat hazardous and radioactive wastes. Two steam reforming



systems, one by the Scientific Ecology Group (SEG) and the other by ThermoChem, Inc., are described. In both systems, steam reforming (a) is performed at atmospheric pressure, (b) significantly reduces waste volume, and (c) takes place in a low oxygen, reducing environment to avoid production of dioxins and furans.

Now owned by SEG, Thermolytica and Synthetica Technologies, Inc. pioneered and patented steam reforming systems for treating hazardous and radioactive wastes using a two-stage operation (Galloway 1987; Galloway 1989). In the first stage, organics are vaporized and decomposed by superheated steam at temperatures between 320°C (600°F) and 600°C (1,100°F). In the second stage, the first-stage offgas is mixed with superheated steam at a nominal temperature of 1,100°C (2,000°F) to complete organic decomposition and the formation of syngas and other useful gaseous products. For organic solvents found in mixed wastes, destruction efficiencies between 99.99% and 99.9999% can be achieved by varying the second-stage temperature from 1,000°C (1,800°F) to 1,200°C (2,200°F). Also, radioactive treatment applications have been addressed (Galloway et al. 1994). For nitrate-mixed waste destruction, Resources Conservation and Recovery Act (RCRA) organic destruction requirements are met, plus over 92% destruction efficiencies of the nitrates have been demonstrated (Galloway et al. 1993). Metals and other inorganic residues in the waste feeds are partitioned and isolated in the first stage for direct disposal, solidification, or reuse.

In 1995, SEG, a wholly-owned subsidiary of Westinghouse Electric Corporation, acquired Synthetica Technologies, Inc., including the early work of Thermolytica. SEG now holds the entire patent portfolio for steam-reforming waste processing and manufacturing of Synthetica steam reforming units for commercial activities. The US EPA classifies SEG technology as a non-incineration technology. The SEG technology is available as fixed or mobile units.

SEG has provided demonstrations for DOE-sponsored tests with Sandia National Laboratories (Miller et al. 1995). It recently completed an eight-month waste treatment contract for about 230 m<sup>3</sup> (300 yd<sup>3</sup>) of nuclear power plant radioactive waste containing heavy metals. SEG now operates a dual feed (drum or shredder/ heated screw) commercialized unit for treatment of a variety of radioactive, mixed radioactive and hazardous, and halogenated wastes, including bio-pharmaceutical and research laboratory radioactive wastes. These wastes have elevated levels of chlorine and fluorine that are being handled by a proprietary SEG process that produces inert salt

disposal products. Other treatment contracts exist with the Trojan Nuclear Power Plant, and with DOE's Rocky Flats Plant in Colorado and the Idaho National Engineering Laboratory in Idaho.

The ThermoChem system (DOE 1996) consists mainly of a solid/liquid continuous feed system, a first and a second stage steam reformer, and a flameless thermal oxidizer. The first stage steam reformer is an indirectly heated fluidized bed in a refractory-lined reactor vessel. The fluidized bed temperature (480 to 650°C [900 to 1,200°F]) is closely controlled to ensure complete volatilization and partial steam reforming of all organic compounds. The temperature is also kept sufficiently low to ensure retention of radionuclides in the bed material and retention of inorganic materials in the first stage. Radionuclides and inorganic materials are continuously removed from the first stage for final disposal. Product gases from the first stage are routed to the second stage where greater destruction efficiencies can be achieved, if required. Otherwise, the second stage can be bypassed.

Product gases, either from the first or second stage, are routed to a flameless thermal oxidizer where hydrocarbon vapors are converted to carbon dioxide, water, hydrogen chloride, and sulfur dioxide. Outputs from the oxidizer are routed through a hot gas scrubber and filtration system and then released. Laboratory testing indicates that 99.9999% organic destruction efficiencies can be achieved with the ThermoChem system. This testing has included naphthalene, dichlorobenzene, toluene, phenol, tetrachloroethylene, vinyl chloride, trichloroethylene, and ethylene glycol. Additional tests have been conducted using feed sludge from paper mill waste containing dioxins (AghaMohammadi 1995).

ThermoChem is under contract to design, build, and operate a nominal 45 kg/hr (100 lb/hr) Process Development Unit (PDU). The PDU will be tested using six surrogate feedstocks that are representative of DOE mixed low level waste. Preliminary screening tests were conducted at Sandia National Laboratories with a single-stage (fluidized bed) unit operating at 900°C (1,650°F) (AghaMohammadi 1995). Destruction efficiencies in this test ranged from greater than 99.99% for tetrachloroethylene to an average of 98.48% for 1,2-Dichlorobenzene. Plans are to conduct additional testing with a two-stage, 1.1 tonne/day (1.2 ton/day) unit.

## ***Plasma Torch and Electric Arc Technologies***

Plasma torch and electric arc technologies are alternating or direct current electrical heating processes (Schwinkendorf et al. 1995; DoD 1995). They are adaptations of foundry technologies and rely on high energy electrical discharges to convert a gas into a high-temperature plasma. The plasma torch functions in a flowing gas medium while the electric arc functions in a static gas medium. Although centerline plasma temperatures may reach 12,000°C (22,000°F) or more, plasma surface and surrounding gas temperatures vary between 1,500°C (2,700°F) and 5,300°C (9,600°F). Heat transfer to the waste material in the primary reactor hearth is primarily by radiation with some contribution by convection from the surrounding gas. In addition, joule heating occurs when the waste material is used as one of the electrodes. Generally, these systems can accept a variety of input wastes materials, even "as received" in their original containers.

The plasma torch and electric arc systems volatilize and decompose organic materials and melt inorganic materials into a glassy slag, and in some cases, into a separate molten metal phase. Offgas processing systems are provided to ensure complete combustion of combustible gases and volatilized organics. When withdrawn, the slag forms a leach-resistant vitrified (glassy) waste form that is suitable for disposal. The molten metal phase, if formed, can be withdrawn separately and recycled for alternate uses of the recovered metal.

Plasma torch and electric arc technologies are similar. Laboratory, pilot, and demonstration units are being developed by several companies, alone and in conjunction with DOE and DOE national laboratories. Some companies have commercialized and are applying these technologies for the treatment of hazardous wastes. Preparations for mixed radioactive and hazardous waste testing are underway.

DOE has sponsored development, test, and evaluation of the Plasma Hearth Process (PHP), a non-radioactive, fixed hearth, plasma torch system, at both the laboratory- and pilot-scale (DOE 1994a; DOE 1994c). In addition, Science Applications International Corporation (SAIC) operates a 200 KW nonradioactive fixed hearth plasma process at its Science and Technology Applications Research (STAR) Center in Idaho. A pilot-scale,

## Other Promising Technologies

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non-radioactive PHP system will be constructed at Retech, Inc. in Ukiah, California. A bench-scale radioactive PHP system is being installed in the Argonne National Laboratory West (ANL-W) Transient Reactor Test (TREAT) facility in Idaho (DOE 1995b).

Retech, Inc. has also developed the Plasma Arc Centrifugal Treatment (PACT) system, a rotating-tub (hearth), plasma torch system. Several sizes, ranging from 46 cm (1.5 ft) to 244 cm (8 ft) in diameter have been tested. A 183 cm (6 ft), 136 kg/hr (300 lb/hr) design has been used in DOE-sponsored tests at the Component Development and Integration Facility (CDIF) in Butte, Montana, to demonstrate its application in the treatment of mixed wastes at the Idaho National Engineering Laboratory (INEL). Two systems are operating in Switzerland and one in France. Retech also built the bench-scale PHP unit for the ANL-W radioactive waste demonstration project. Two PACT systems for treatability studies are located at Retech's Ukiah facility and a third one is under construction (Eschenback et al. 1993). In early 1996, Retech, Inc. was acquired by M4 Environmental L.P., Oak Ridge, Tennessee.

Plasma Energy Applied Technology (PEAT), Inc., Huntsville, Alabama, has developed a single stage, plasma torch Thermal Destruction and Recovery (TDR) patented system for treating mixed hazardous and radioactive wastes. Steam, oxygen, or air is injected into the reactor vessel to enhance organic destruction efficiencies. Temperatures within the reaction vessel are often over 1,650°C (3,000°F). Inorganics are either recovered or immobilized for disposal. Gaseous products are similar to other plasma torch processes, are relatively free of dioxins and furans, and are scrubbed before they are released. An "Authority to Construct" has been issued by the San Diego County Air Pollution Control District to install a TDR system for processing medical waste at the Kaiser Permanente Medical Center in San Diego, California. However, its implementation has been delayed pending results of additional cost benefit analyses. A contract is in place with Allied Technology Group (ATG), Richland, Washington, to provide a TDR system for treating mixed, low-level waste from DOE's Hanford facility.

Other plasma torch systems are under various stages of development include:

- Plasma Technology, Inc., Santa Fe, New Mexico, has developed and is marketing a Plasma Energy Recycle and Conversion (PERC™) process that uses electrodeless Induction Coupled Plasma (ICP) torches that provide a wide range of plasma gases.

A commercial PERC™ system has been installed for Alliant Techsystems in Elk River, Minnesota, to treat energetic materials and chemical warfare agents. Initial operations were completed in September, 1995 (Blutke et al. 1995).

- INEL has developed a hybrid steam plasma technology that has two plasma sources operated in tandem. Bench-scale demonstrations have been completed on liquid organics and black liquor waste from the wood pulping process (DOE 1994b).
- Westinghouse Electric Corporation under Electric Power Research Institute (EPRI) sponsorship has developed a plasma cupola technology that is now being marketed by Westinghouse (Dighe et al. 1991).

Two electric arc systems have been tested and demonstrated. One is the graphite electrode direct current arc system, demonstrated in both the Mark I, 0.3 MW furnace (Surma et al. 1993) and the larger Mark II, 1 MW furnace (DOE 1994a). A Mark I unit is currently being used at the Clemson Vitrification Research Laboratory, Clemson, South Carolina (Erich and Overcamp 1996). These furnaces, based on Electro-Pyrolysis technology, were jointly developed and demonstrated by Pacific Northwest Laboratory (PNL), Massachusetts Institute of Technology (MIT), and Electro-Pyrolysis Inc. with funding support from DOE. These systems are now being marketed by Svedala Industries, Pyro Systems Division, Waukesha, Wisconsin, a unit of Sweden's Svedala Industries, Inc. (Trescot et al 1995).

The second electric arc system is the alternating current graphite electrode arc melter. Development of this system has been supported by DOE and is an extension of a U.S. Bureau of Mines (USBM) and American Society of Mechanical Engineers (ASME) demonstration of the vitrification of municipal waste combustor residues (DOE 1994a; American Society of Mechanical Engineers 1994). The furnace, developed in cooperation with Lectromelt, a subdivision of the Salem Furnace Company, is a sealed, 800 kVA (0.8 MW) arc furnace. It is generally operated between 350 and 550 kW in power. This unit has recently been used to treat simulated transuranic (TRU) contaminated waste and soils, and high sodium, low-level radioactive liquid tank waste by encapsulating the TRU contaminants in a glass/ceramic waste form (O'Connor et al. 1996; O'Connor et al. 1995; Soelberg et al. 1994).

## ***Horsehead Resource Development Company Flame Reactor***

The Flame Reactor is a high-temperature metal recovery process that destroys organics, extracts metals, and vitrifies contaminants. It consists of a burner stage (fuel combustion) and a reactor stage (oxide reduction). It can be used to treat sludges, slags, and soils and recover metals in these wastes for recycling. Three large-scale tests have been conducted and show that organic destruction efficiency exceeds 99.99% for  $\text{CCl}_4$ , metal recovery efficiencies range up to 92%, and the solidified slag consistently passes TCLP testing.

Electric Arc Furnace (EAF) steelmakers in the United States generate approximately 545,450 tonne (600,000 ton) of hazardous EAF flue dusts annually. Most of the dust is processed at large regional facilities to recover marketable metal products (e.g., lead, cadmium, zinc, copper, and nickel) for recycling. A smaller gas-fired Flame Reactor has been developed under sponsorship of the Gas Research Institute (GRI). This unit is intended for on-site applications at new "mini-mills" and existing facilities remote from a regional facility (Natural Gas Applications in Industry 1994).

Pilot plant tests for small-scale Flame Reactor have been completed on more than 3,600 tonne (4,000 ton) of various wastes. A commercial, 27,300 tonne/yr (30,000 ton/yr) facility has been permitted and started operations in Beaumont, Texas, in 1993. Other facilities are under consideration. With GRI support, Horsehead is investigating alternative waste applications for the gas-fired Flame Reactor. Included are electroplating wastes, lead-contaminated soils, hazardous waste incinerator ash, and secondary copper and brass foundry wastes (Clark et al. 1994).

## ***Systems Engineering Analysis***

DOE has taken an overall systems view in applying technologies for treatment of mixed waste. A study was conducted of thermal treatment systems in which nineteen system options using varied technologies were considered. System options were compared for costs, effluents, and amounts of final residue for disposal. The thermal study results emphasized the importance

of reducing characterization and pretreatment, operating and maintenance, and disposal costs. All types of wastes were processed within the same facility. Where only 20% of the total waste mass was combustible, the overall costs were rather insensitive to the type of thermal treatment (Feizollahi et al. 1995; Cudahy et al. 1995).

A similar study of nonthermal (operating temperatures less than 350°C [660°F]) treatment systems was also conducted in which five system options using varied nonthermal technologies were considered (Biagi et al. 1996). Major conclusions are that:

- gas emissions from nonthermal systems are significantly less than those from thermal systems;
- waste form volumes for disposal are generally greater for nonthermal systems;
- technology maturity levels are generally less than for nonthermal technologies; and
- nonthermal systems tend to be more expensive than thermal systems (Schwinkendorf 1996).

姓名	性别	年龄	籍贯	职业	文化程度	政治面貌	健康状况	婚姻状况	子女情况	其他
王德胜	男	45	山东	工人	小学	党员	良好	已婚	2子1女	
李秀英	女	38	河北	农民	初中	团员	良好	已婚	1子1女	
张国强	男	52	河南	干部	高中	党员	良好	已婚	2子1女	
刘小红	女	28	江苏	教师	大学	党员	良好	已婚	1子1女	
陈为民	男	40	浙江	商人	小学	无党派	良好	已婚	2子1女	
赵大刚	男	35	湖北	工人	初中	团员	良好	已婚	1子1女	
孙丽娟	女	32	湖南	农民	小学	无党派	良好	已婚	2子1女	
周建民	男	48	四川	干部	高中	党员	良好	已婚	2子1女	
吴小芳	女	25	广东	教师	大学	党员	良好	已婚	1子1女	
郑为民	男	50	广西	商人	小学	无党派	良好	已婚	2子1女	
冯大刚	男	38	福建	工人	初中	团员	良好	已婚	1子1女	
李秀英	女	30	江西	农民	小学	无党派	良好	已婚	2子1女	
周建民	男	42	安徽	干部	高中	党员	良好	已婚	2子1女	
吴小芳	女	28	山西	教师	大学	党员	良好	已婚	1子1女	
郑为民	男	45	陕西	商人	小学	无党派	良好	已婚	2子1女	
冯大刚	男	35	甘肃	工人	初中	团员	良好	已婚	1子1女	
李秀英	女	32	宁夏	农民	小学	无党派	良好	已婚	2子1女	
周建民	男	48	青海	干部	高中	党员	良好	已婚	2子1女	
吴小芳	女	25	新疆	教师	大学	党员	良好	已婚	1子1女	
郑为民	男	50	内蒙古	商人	小学	无党派	良好	已婚	2子1女	
冯大刚	男	38	黑龙江	工人	初中	团员	良好	已婚	1子1女	
李秀英	女	30	吉林	农民	小学	无党派	良好	已婚	2子1女	
周建民	男	42	辽宁	干部	高中	党员	良好	已婚	2子1女	
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李秀英	女	32	山西	农民	小学	无党派	良好	已婚	2子1女	
周建民	男	48	陕西	干部	高中	党员	良好	已婚	2子1女	
吴小芳	女	25	甘肃	教师	大学	党员	良好	已婚	1子1女	
郑为民	男	50	宁夏	商人	小学	无党派	良好	已婚	2子1女	
冯大刚	男	38	青海	工人	初中	团员	良好	已婚	1子1女	
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周美兰	女	35	湖南	护士	高中	良好	已婚	1子	
吴建国	男	55	安徽	工人	小学	良好	已婚	3子	
孙文娟	女	28	湖北	学生	初中	良好	未婚	0子	
郑大刚	男	42	江西	农民	文盲	良好	已婚	2子	
冯小芳	女	32	广东	家庭主妇	小学	良好	已婚	1子	
马长贵	男	50	广西	工人	小学	良好	已婚	3子	
朱小红	女	22	福建	学生	初中	良好	未婚	0子	
徐大伟	男	38	山西	商人	小学	良好	已婚	2子	
周美兰	女	35	湖南	护士	高中	良好	已婚	1子	
吴建国	男	55	安徽	工人	小学	良好	已婚	3子	
孙文娟	女	28	湖北	学生	初中	良好	未婚	0子	
郑大刚	男	42	江西	农民	文盲	良好	已婚	2子	
冯小芳	女	32	广东	家庭主妇	小学	良好	已婚	1子	
马长贵	男	50	广西	工人	小学	良好	已婚	3子	
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孙文娟	女	28	湖北	学生	初中	良好	未婚	0子	
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