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TREATMENT OF PULP MILL SLUDGES BY SUPERCRITICAL WATER OXIDATION

Final Report

By
Michael Modell

July 1990

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ABSTRACT

Supercritical water oxidation (SCWO) is a new process that can oxidize organics very effectively at moderate temperatures (400 to 650°C) and high pressure (3700 psi). It is an environmentally acceptable alternative for sludge treatment. In bench scale tests, total organic carbon (TOC) and total organic halide (TOX) reductions of 99 to 99.9% were obtained; dioxin reductions were 95 to 99.9%. A conceptual design for commercial systems has been completed and preliminary economics have been estimated. Comparisons confirm that SCWO is less costly than dewatering plus incineration for treating pulp mill sludges. SCWO can also compete effectively with dewatering plus landfilling where tipping fees exceed $35/yd^3$. In some regions of the U.S., tipping fees are now $75/yd^3$ and rising steadily. In the 1995 to 2000 time frame, SCWO has a good chance of becoming the method of choice. MODEC's objective is to bring the technology to commercial availability by 1993.

I. SUMMARY

A. Background

Pulp mill sludge disposal practice has traditionally been dependent upon landfilling and land-farming. Environmental concerns have led to: (i) growing pressures to decrease land-based disposal practices and (ii) increasing costs to permit and install state-of-the-art landfills. Exacerbating the problem are the recent findings that dioxins and furans are present in pulp mill effluents, including sludges. Although dioxin production can be reduced significantly by modest changes in the bleaching process, reduction in total organic halide (TOX) emission may be the more difficult challenge. There is a consensus emerging that land disposal of pulp mill sludges is becoming more problematic and may cease to be an available option in the not too distant future.

Today, the only acceptable alternative to land disposal is combustion. Burning a wet sludge in a boiler requires addition of auxiliary fuel and/or derating the boiler.

The trend in sludge oxidation practice is to use incinerators rather than bark boilers and to use high temperature, rotary kiln incinerators rather than intermediate temperature fluidized bed incinerators. To reach peak temperatures of 1000 to 1100°C, a pulp mill sludge with 40 wt-% solids would require addition of 4,000 to 5,000 Btu per lb of sludge.

Supercritical water oxidation (SCWO) is an environmentally acceptable alternative for sludge disposal. It is less costly than incineration because it uses regenerative heat exchange to preheat feed and cool effluents. With a feed concentration of 10 wt-% solids, not only can sludges be oxidized without addition of auxiliary fuel, but over 45% of the sludge heating value can be recovered as steam. With residence times on the order of 5 to 10 minutes, oxidation efficiencies greater than 99% can be obtained and, thus, effluents can be exceptionally clean.

MODEC has achieved several technical breakthroughs that have overcome the prior barriers to commercializing SCWO: reactors and components which do not plug with inorganic solids; and removal of inorganic solids from the high pressure system without disruption of the process. MODEC has demonstrated these innovations on a bench scale prototype that simulates commercial scale operation.

Under DOE/Office of Industrial Programs (OIP) sponsorship, MODEC has recently completed an assessment of SCWO for treating pulp mill sludges.

Reported herein are the results of bench scale tests and preliminary process design. Cost comparisons to landfilling and incineration are also included.

B. Supercritical Water Oxidation

SCWO is a process for oxidizing organic materials, thereby converting them to carbon dioxide, and inorganic acids. The overall chemical transformations are analogous to those in incineration, but the way in which the oxidation is conducted is very different. Unlike incineration, SCWO is conducted at mild temperatures (400 to 650°C), where many alloys maintain mechanical strength. Instead of ultrafast reaction in an inherently unstable flame, SCWO takes minutes to complete, but in a stable, plug-flow reactor. The oxidation zone occupies the whole reactor; waste cannot short-circuit or bypass the oxidation zone.

At atmospheric pressure, it is not possible to oxidize organics at 400 to 650°C. Before they oxidize, organics usually char, and char burns effectively only at high temperature. Oxidation at the mild temperatures of SCWO conditions is made possible by high pressure and the presence of water as the reaction medium. Water above 374°C and 3200 psi is a supercritical fluid. In that state, supercritical water (SCW) becomes a superb solvent for organic materials as well as gases. In addition, SCW reacts with organics and reforms them to small molecules - without the formation of char (Modell, 1985(1)). These small molecules are readily oxidized if air or oxygen is mixed with the organic-SCW mixture.

A flowsheet of MODEC's SCWO process for pulp mill sludge is shown in Figure S1. It is designed to process a sludge with 10 wt-% solids (primary or secondary or mixed), producing clean effluents: a gas which is primarily carbon dioxide (95 to 99.95% CO_2, the balance being O_2, with small amounts of N_2), a liquid which is clean water with some dissolved alkali salts, and a solid which is primarily oxides and insoluble salts of metals contained in the sludge.

The major features of MODEC's SCWO process for treatment of pulp mill sludges are as follows:

- oxidation at 550 to 650°C provides greater than 99% combustion efficiency and effective destruction of chlorinated organics, including dioxins;
- sludge can be fed at 10 wt-% solids, thereby eliminating the need for extensive and costly dewatering;

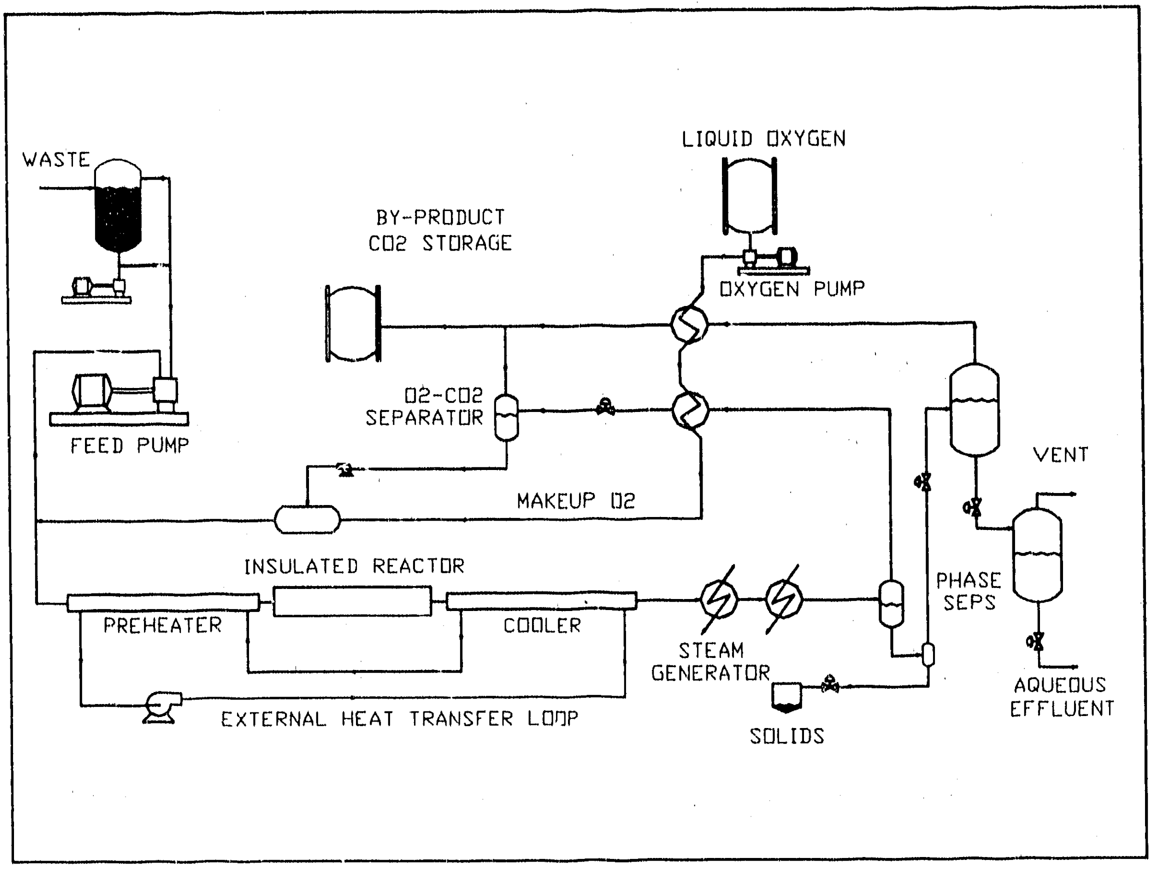


FIGURE S1. MODEC'S PROCESS FOR SCWO TREATMENT OF PULP MILL SLUDGE

- regenerative heat exchange is used to preheat the feed, thereby eliminating the need for auxiliary fuels to sustain combustion;
- more than 45% of the sludge heating value is recovered as steam, which can be used in the pulp mill to offset prime energy consumption;
- carbon dioxide can be recovered in pure enough form to provide a substantial by-product credit;
- liquefaction of carbon dioxide eliminates the possibility of uncontrolled emissions and paves the way to rapid acceptability.

C. SCWO Bench Scale Tests

The objective of these tests was to determine if SCWO can effectively oxidize the organic matter in pulp mill sludges, including dioxin constituents. Two sludge samples from operating pulp mills were obtained and tested: one was supplied by the National Council on Air and Stream Improvement (NCASI) and one was obtained by MODEC from a pulp and paper company (herein identified as "Company X"). Both were mixtures of primary and secondary sludge, containing about 70:30 organic-to-inorganic components.

The tests were performed on MODEC's bench scale SCWO unit, which is also used to gather design data. It simulates the time-temperature history that a waste would experience in a commercial scale system. The unit is capable of processing an aqueous feed of up to 80 cc/min (30 GPD), containing up to 3,000 Btu/lb with up to 10 wt-% solids of particles less than 100 micron. Reactor operating limits for pulp mill sludge are presently 600°C and 3700 psi. Residence times can range from 10 seconds to 10 minutes.

The bench scale test results show that SCWO provides effective destruction of organics at 550 to 600°C. Highlights are as follows:

- total organic carbon destruction efficiencies of 99% were obtained;
- organic chloride destruction efficiencies exceeded 99.9%;
- dioxin destruction/reduction efficiencies ranged from 96.7% for a sludge with 0.34 parts per trillion to >99.98% for a sludge with 123 parts per trillion;
- the liquid effluent is water that is clean enough to be reused in the mill;
- the inorganic solid effluent is clean enough to be sent to a sanitary landfill.

D. Economic Comparisons

A cost comparison was made for a pulp mill producing 100 dry ton/day of mixed primary and secondary sludge. Three alternatives are considered:

(i) Dewatering with screw presses to 40 wt-% solids, followed by trucking of the sludge to a nearby landfill;

TABLE S1. 100 TPD COST COMPARISONS FOR CASES 1 AND 2

Assumptions	Tipping Fee ($/yd ^{3})	Fuel Cost ($/MBtu)	Power Cost ($/KwH)
Case 1	35	5	0.05
Case 2	10	3	0.03

Option:	Dewater to 40% Solids + Landfill	Dewater to 40% Solids + Incinerate	Dewater to 10% Solids + SCWO
Case 1			
Capital Cost	$4,000,000	$21,000,000	$20,200,000
Annual O&M Cost	7,070,000	8,015,000	2,017,000
Unit Cost ($/bone dry ton)	213	330	160
Case 2			
Capital Cost	$4,000,000	$21,000,000	$20,200,000
Annual O&M Cost	3,395,000	6,310,000	1,696,000
Unit Cost ($/bone dry ton)	108	275	151

(ii) Dewatering with screw presses to 40 wt-% solids, followed by on-site incineration at 1100°C; or

(iii) Dewatering with a centrifuge to 10 wt-% solids, followed by on-site SCWO treatment.

To reflect regional differences throughout the U.S., two cases are considered, each with different parameters for tipping fees, fuel and electricity costs. The parameters, shown in Table S1, might reflect conditions in the northeast or midwest (Case 1) and the northwest or southeast (Case 2). Installed capital costs, annual operating and maintenance (O&M) costs, and unit costs are shown in Table S1.

Cases 1 and 2 show that SCWO is clearly more cost-effective than incineration. Given that the capital costs of the two are comparable, the only advantage incineration has is that it is already available commercially.

With respect to landfilling, an investment analysis is required to determine the rate of return on the additional capital cost of the SCWO system versus the savings in O&M cost. Such an analysis was conducted for a scenario of a large mill in the northeast or midwest (Case 1) facing a decision on sludge disposal for 1995. Even with a conservative life of 10 years, the SCWO option can return 25% on the investment of added capital above the landfilling option. Thus, MODEC anticipates that large pulp and paper companies with extensive operations in the northeast or midwest are potential clients for first generation 100 TPD systems.

The costs for Case 2 (Table S1) show that landfills will continue to be the most economical alternative as long as tipping fees in the range of $10/yd^3$ are available. For large mills in the northwest and southeast, the only incentive to seek oxidation alternatives is the need to keep one's options open in the face of unpredictable regulations governing land disposal. When oxidation options are sought, it is clear that SCWO is far more cost-effective than incineration.

E. Conclusions

In the future, sludges will undoubtedly have to be treated rather than disposed of in the ocean or on land. Incineration, the only treatment process available commercially today, consumes large quantities of auxiliary fuel and is expensive.

SCWO is more energy-efficient, cost-effective and environmentally-acceptable than incineration for industrial and municipal sludges. MODEC has developed non-plugging reactors and effective means of separating inorganic solids from clean aqueous effluent. MODEC intends to demonstrate its process for pulp mill sludge then commercialize it by 1993.

II. INTRODUCTION

Sludge is a ubiquitous by-product of wastewater treatment. The U.S. leads the world in sludge generation because the U.S. leads the world in requirements for wastewater treatment. Over the past twenty-five years, the permissible levels of contaminants in aqueous effluents discharged to the environment have decreased significantly. Today, almost every U.S. industry that uses large quantities of water treats the effluent to some degree and generates a sludge in the process.

As the amount of sludge generated has increased, concern over how it is disposed has also grown. In fact, sludge disposal is rapidly becoming a pressing problem for U.S. industry, in general, and for the pulp and paper industry, in particular. Current practice relies heavily on land-based methods, with landfill disposal heading the list. Landfills are getting more difficult to permit and more costly to operate.

Land-based disposal does not significantly alter the chemical or physical characteristics of the sludge. Oxidation, on the other hand, destroys the bacteria, converts organic material to carbon dioxide and water, and produces a compact residue of inorganic ash. At present, the only commercially available alternative for oxidizing sludge is incineration, which is costly and energy-intensive.

The pulp and paper industry is now faced with a potentially acute sludge problem. In recent years, dioxins have been found in sludges generated at pulp mills using chlorine-based chemicals for bleaching. Although dioxin production can be reduced significantly by modest changes in the bleaching process, reduction in total organic halide (TOX) emission may be the more difficult challenge to land disposal practice. Since many organic chlorides are considered toxic, there is the possibility that TOX-containing sludges might be reclassified as a hazardous waste, which would mean that *secured* landfills will be required and the disposal costs would be substantially higher.

Supercritical water oxidation (SCWO) is a cost-effective, environmentally-sound method of treating sludges from industrial wastewater treatment. Modell Development Corporation (MODEC) has shown that SCWO can effectively oxidize municipal sewage sludge to benign products (CO_2 and clean ash). The purpose of this project was to extend MODEC's prior work on sewage sludges to pulp mill sludges containing dioxins. This report describes the results of bench scale tests for SCWO treatment of pulp mill sludges. Destruction efficiencies of 2,3,7,8-tetrachlorodibenzodioxin (2,3,7,8-TCDD) and 2,3,7,8-tetrachlorodibenzofuran

(2,3,7,8-TCDF) were measured and are reported herein. In addition, results of a test made with pure 2,3,7,8-TCDD are given.

Conceptual design of a full scale SCWO system for pulp mill sludge is presented, along with capital and operating cost estimates for various throughputs. Finally, cost comparisons are shown for SCWO, incineration, and landfilling.

III. BACKGROUND

In this section, background information on sludges is provided. Estimates of the costs of dewatering, followed by landfilling or incineration are presented. Background information on supercritical water oxidation is presented in Section IV.

A. SLUDGE GENERATION AND DISPOSAL

Wastes are usually categorized as either 'wastewater' or 'solid waste'; both terms are used very loosely. Wastewater is any waste that is predominantly water (>50%), while solid waste is everything else (including liquid wastes and refuse).

'Sludge' is a generic term, also used loosely, associated with wastes that are predominantly water, contain organic and inorganic matter, and have a color of gray to black. Sludges are generated by every industry that uses large quantities of water. Figure 1 illustrates how sludges arise within a typical wastewater treatment train. The three treatment steps are as follows:

Pretreatment. Large particulate matter is first removed by screens.

Primary treatment. The concentration of small particles, measured as total suspended solids (TSS), is reduced by settling and flotation. The wet solids so removed are called a primary sludge.

Secondary treatment. An increasing number of wastewater treatment facilities follow primary treatment by a secondary treatment to reduce biological oxygen demand (BOD). Dissolved organic matter is consumed by bacteria and converted to carbon dioxide (by digestion) and more bacteria (by reproduction). The excess bacteria is removed as the secondary sludge.

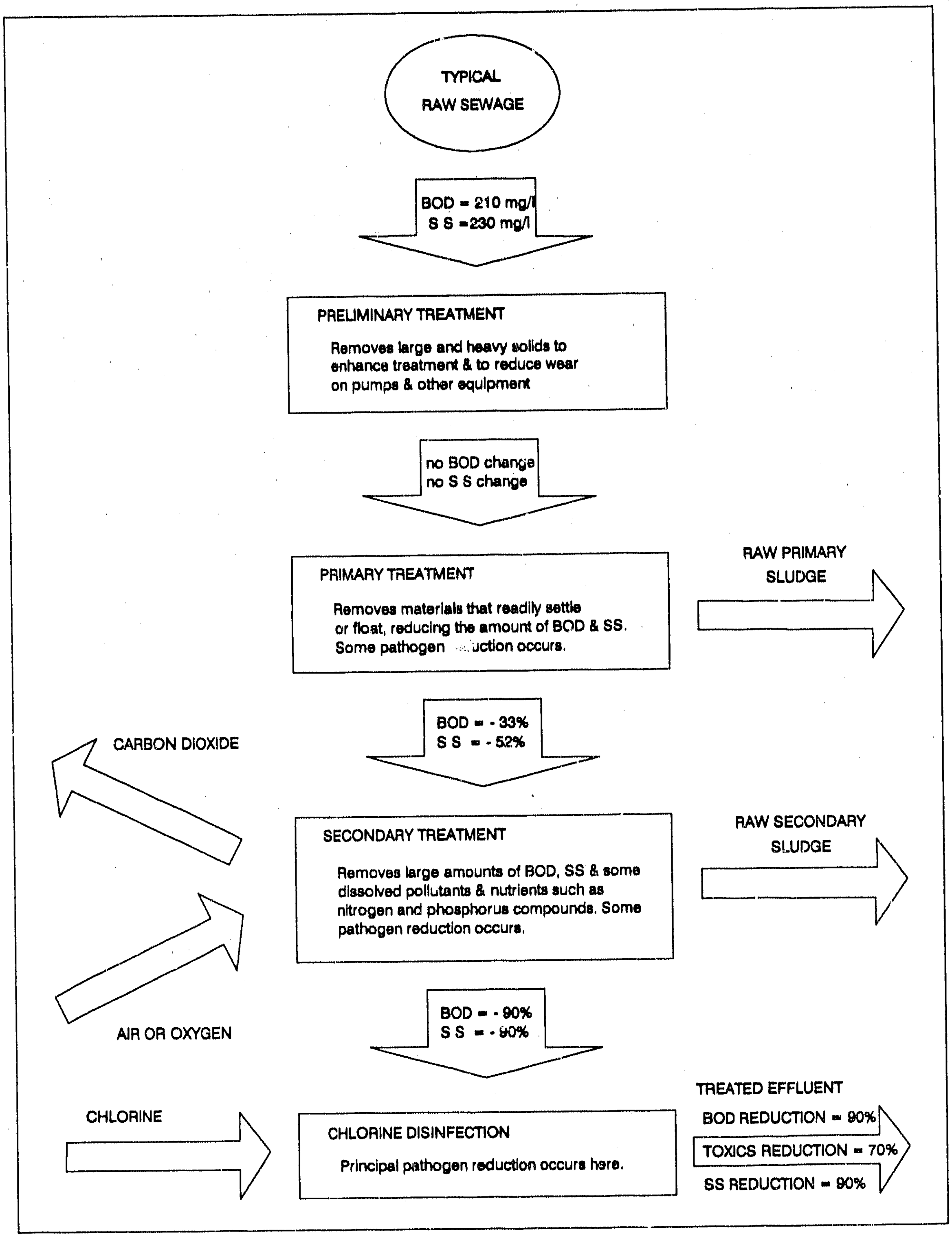


FIGURE 1. A TYPICAL MUNICIPAL SEWAGE TREATMENT TRAIN

TABLE 1. QUANTITIES OF SOME SLUDGES PRODUCED IN THE U.S.

Source	Quantity (wet tons/yr)	Solids Content (wt-%)
Municipal sewage treatment works	300 million	3
Chemical-related industries	250 million	1 to 10
Pulp and paper industry	100 million	3

Thus, sludge is the residue or by-product from treatment of raw aqueous waste. Table 1 provides some order-of-magnitude estimates of the quantities of sludges generated by various industries.

A common characteristic of sludges is that *they are difficult and costly to dewater.* When initially produced or collected, they are very dilute (0.5 to 5 wt-% solids). They usually contain colloidal solids and/or bacterial mass that holds onto water tenaciously. Sludges can be concentrated or dewatered to varying degrees, but rarely to more than 45% solids. Ordinary filtration without pretreatment is not effective. Table 2 lists some common dewatering methods and the concentrations of solids produced by them. Figure 2 is a schematic of the steps involved in screw press filtration for dewatering a pulp mill sludge to 40 wt-% solids.

The water content of a sludge is a key factor in determining the cost of disposal. The predominant methods of disposal have been - and are still - dumping the sludges on land (e.g., landfilling and 'land-farming') or in the ocean. The total disposal cost is the sum of the costs of dewatering, transportation, and dump site tipping fee. The transportation and tipping costs are proportional to volume of the sludge mass (i.e.,

TABLE 2. METHODS OF DEWATERING SLUDGES

Process/Equipment	Pretreatment	Final Solids (wt-%)
Centrifugation	None	5-10
Centrifugation	Coagulants	10-20
Vacuum filtration	Coagulants	15-25
Belt press filtration	Coagulants	25-35
Screw press filtration	Polymer	35-45

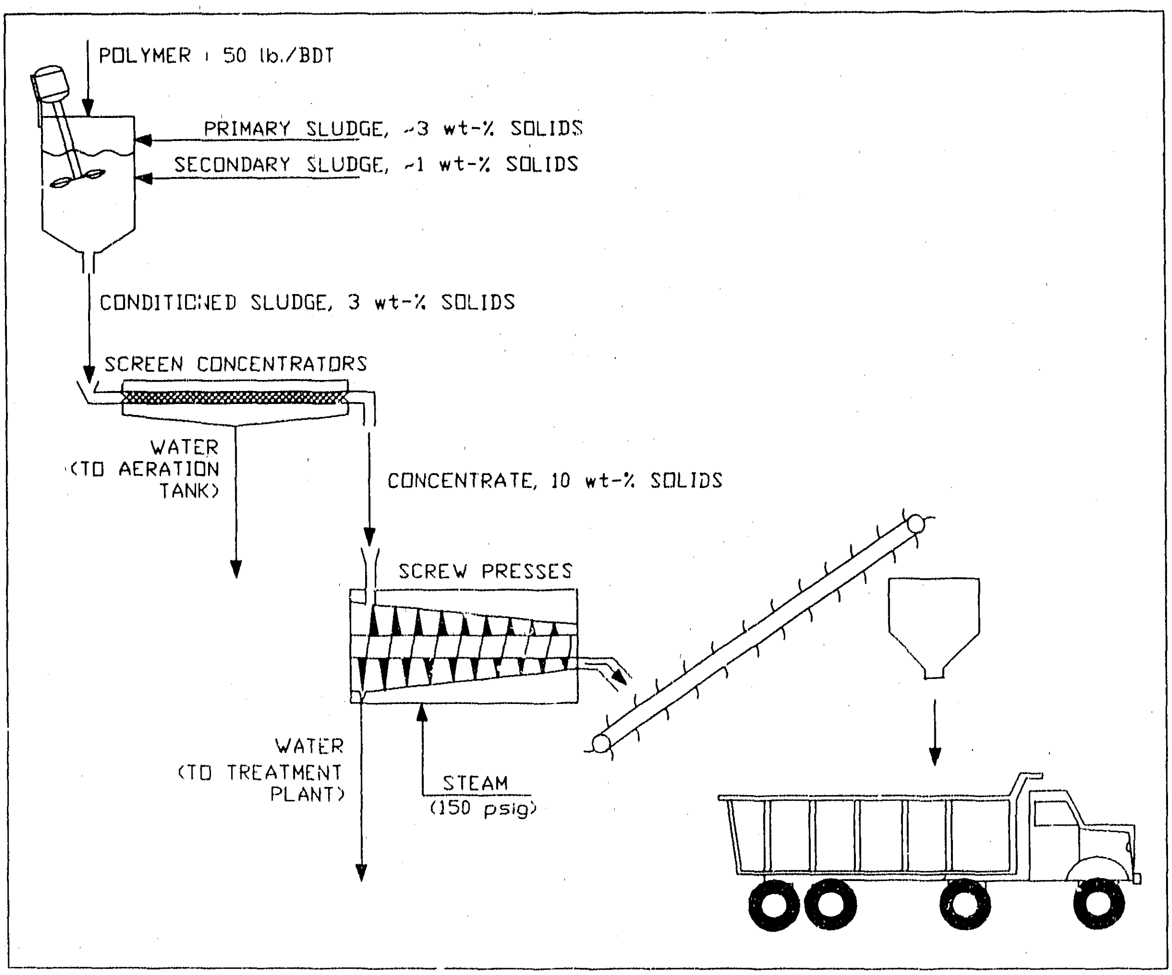


FIGURE 2. SLUDGE DEWATERING BY SCREW PRESS FILTRATION

including the residual water); the unit costs per 'bone dry' ton (BDT) of solids are inversely proportional to solids content. As the tipping fees rise, there is incentive to install dewatering equipment so as to reach an economic optimum of water content.

Table 3 illustrates the interplay of cost factors in dewatering and landfilling. When landfilling tipping fees were $1/yd^3$, it was hard to justify spending capital to dewater beyond 5 to 10% solids. However, $1/yd^3$ tipping fees are gone forever. In the northeast section of the U.S. today, tipping fees range from $35 to 75/yd^3$ and some experts think they will reach $100/yd^3$ before long. In the northwest and south, one can still find landfills in the range of $10/yd^3$, but there too, costs will undoubtedly continue to rise.

TABLE 3. DISPOSAL COSTS FOR DEWATERING AND LANDFILLING SLUDGES

	Solids Content Prior to Landfilling (wt-%)		
	3	20	40
Dewatered Volume (yd^3/BDT)	33	13	4.2
Dewatering O&M Costs ($/BDT)	0	15	55
Capital Cost for Dewatering Equipment** ($M)	0	1	4
Landfill Tipping Fee	O&M Costs for Disposal* ($/BDT)		
$ 1/yd^3	33	28	60
$ 10/yd^3	330	145	100
$ 35/yd^3	1,200	480	200
$ 75/yd^3	2,500	980	370
$ 100/yd^3	3,300	1,300	480

----

*Includes O&M costs for dewatering in-house and tipping fee for landfilling; does not include cost of transporting sludge to landfill.

**Based on 100 bone dry ton (BDT) per day of sludge solids.

Reducing the water content of sludges below 50% usually requires chemical modification. Reduction of total organic carbon (TOC) by partial oxidation can break down the sludge and provide additional alternatives for disposal. For example, the Zimpro process or wet air oxidation (WAO) was used during the 1960's and 1970's to condition sludges. For secondary sewage sludges, TOC reductions of 20 to 40% are sufficient to break down the membranes of bacteria. The effluent from partial oxidation could be filtered and the liquid returned to an activated sludge aeration tank, if one were nearby.[1]

Today, the only acceptable alternative to land disposal is combustion. However, burning a wet sludge in a boiler requires addition of auxiliary fuel and/or derating the boiler. For example, a sewage sludge dewatered to 20 wt-% solids has a heating value of only 400 Btu/lb; a pulp mill sludge at 40 wt-% solids has only 2,800 Btu/lb.

---

[1]Wet air oxidation never captured a significant market share. The process was difficult to operate. Corrosion and fouling were major problems that were not sufficiently resolved. In addition, the solids produced by WAO are odorous and their ultimate disposal is problematic.

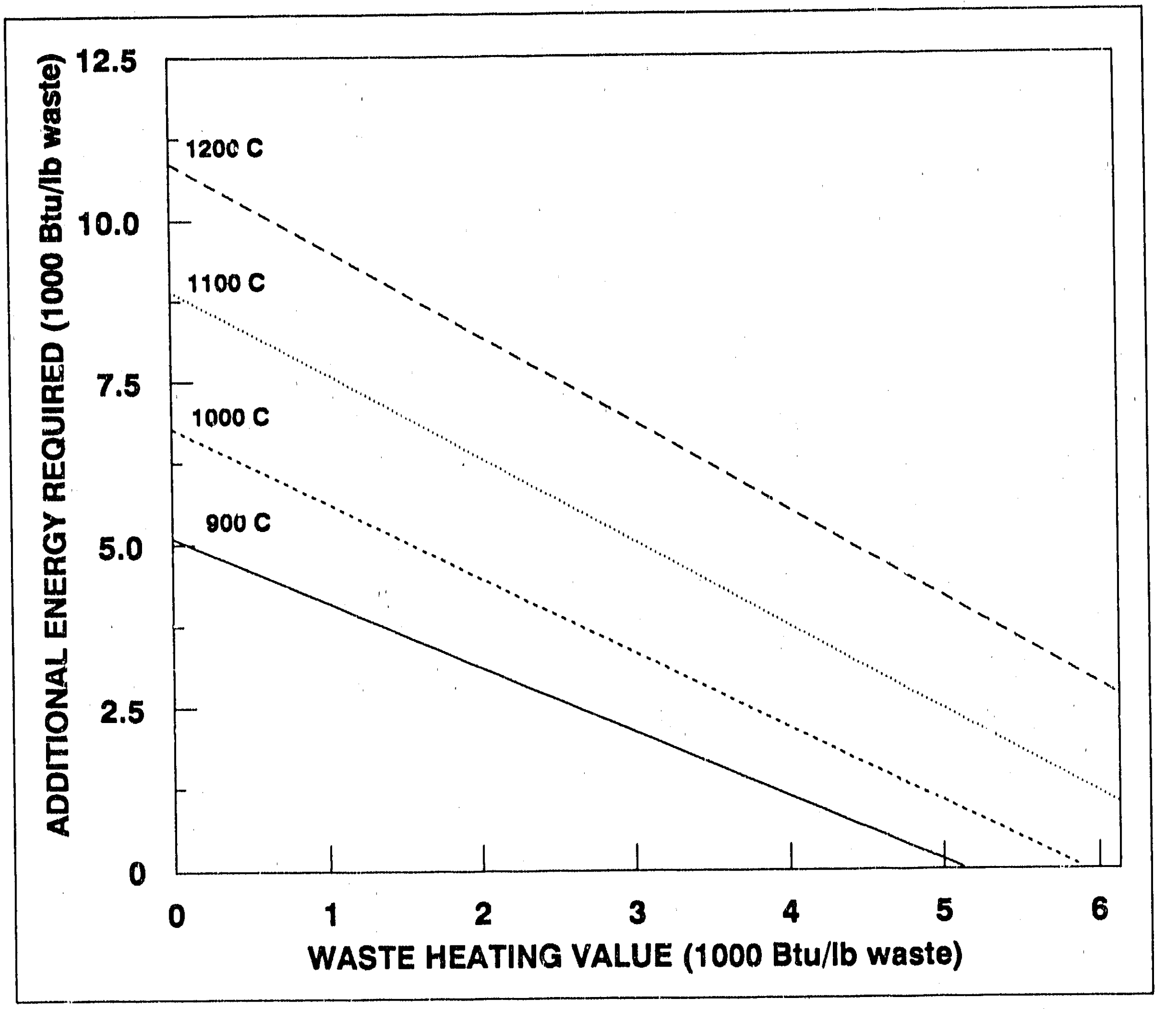


FIGURE 3. ENERGY REQUIRED FOR AQUEOUS WASTE INCINERATION
(7% oxygen in effluent)

The trend in sludge oxidation practice is to use incinerators rather than bark boilers and to use high temperature rotary kiln incinerators rather than intermediate temperature fluidized bed incinerators. MODEC has developed a computer simulation for an incinerator burning an aqueous waste. Auxiliary fuel is co-fired with the aqueous waste so as to reach the desired peak temperature. In Figure 3, the amount of energy required from auxiliary fuel, per ton of the wet waste, is shown as a function of the heating value of the waste and the peak temperature. Where a waste can be burned at 900°C, it is clearly desirable to do so. For example, a fluidized bed combustor burning a very dilute aqueous waste at 900°C, would require addition of 5,000 Btu per pound of waste. A pulp mill sludge with 40 wt-% solids would require about 2,000 Btu per pound of wet sludge at 900°C.

TABLE 4. ESTIMATED COSTS FOR DEWATERING PLUS INCINERATION (100 BDT per day)	
INSTALLED CAPITAL COSTS	$21,000,000
ANNUALIZED COSTS	
Cost of Capital (12%, 10 yr)	$ 3,720,000
Fuel (9×10^{11} Btu/yr @ $3/MBtu)	2,730,000
Labor	580,000
Water	30,000
Chemicals	50,000
Polymer (for dewatering)	1,750,000
Maintenance	460,000
Ash Disposal (7,300 ton/yr @ $30/ton)	220,000
Electric Power (16 KWHr/yr @ $0.03/MWHr)	420,000
Steam (23×10^{3} MBtu/yr @ $3/MBtu)	70,000
Annual Cost	$10,030,000
Unit Cost ($/dry ton)	$275

On the other hand, wastes containing hazardous or toxic components usually require higher temperatures of oxidation. Where wastes contain significant quantities of chlorine compounds, oxidation at 1100 to 1200°C is desirable (if not required) to destroy chlorinated organics (e.g., dioxins, PCB's), or to attain a high degree of combustion so as to minimize the formation of hazardous by-products by recombination of products of incomplete combustion. Since many sludges contain problematic components, there is a trend to use higher temperatures in sludge incinerators. It is not uncommon to find rotary kiln incinerators with stack gas scrubbers being designed to burn pulp mill sludges at 1100°C (2200°F). As can be seen from Figure 3, the penalty in auxiliary fuel costs can be substantial at 1100°C.

MODEC has developed estimates of the cost of incinerating pulp mill sludges at a throughput of 100 BDT per day. It is assumed that the sludge is first dewatered to 40 wt-% solids (by, e.g., addition of polymer and screw press filtration). The combined cost estimates of dewatering and incinerating are given in Table 4. The two major O&M costs are chemicals for dewatering and auxiliary fuel for

TABLE 5. ESTIMATED COSTS FOR INCINERATING SLUDGES AFTER VARYING DEGREES OF DEWATERING

Basis: 100 TPD Incinerator at 1100 ° C

Dewatering Costs

- to 3 wt-% solids: None
- to 20 wt-% solids: $1 Million Installed + $15/BDT O&M
- to 40 wt-% solids: $4 Million Installed + $55/BDT O&M

Incineration Costs

- Installed Capital Cost = $17 Million
- Non-fuel O&M Cost = $44/BDT
- Fuel Costs: From table below

	Fuel Cost for Incineration ($/BDT)	
Wt-% Solids	@ $5/MBtu	@ $3/MBtu
3	$2,860	$1,720
20	350	211
40	130	78

	Total Cost for Dewatering and Incineration ($/BDT)	
Wt-% Solids	@ $5/MBtu	@ $3/MBtu
3	$2,990	$1,850
20	495	360
40	330	275

incineration. The incinerator is assumed to operate at 1100°C with stack gas scrubbers to remove particulate and acid gases. These costs do not include the cost of disposal of the brine from the gas stack scrubber. The fuel costs were based on natural gas, assumed available at $3 per million Btu.

The costs of Table 4 were used to estimate the cost of incineration, following various degrees of dewatering. The results are shown in Table 5 for dewatering to 20 and 40 wt-% solids.. Dewatering to 40 wt-% solids significantly reduces the total cost. Comparing the costs of landfilling (from Table 3) and incineration (from Table 5), it is clear that there is an economic advantage to incinerate when landfill tipping fees exceed $75/yd^3.

B. Pulp Mill Sludges

The trend in sludge production by the U.S. pulp and paper industry is representative of many industrial sectors. All pulp mills generate a primary sludge consisting of fibrous materials that settle out of wastewaters. In an effort to improve the quality of discharged water, a growing number of facilities have installed secondary waste treatment. Bacteria are used to oxidize the biodegradable components of the wastewater. Various forms of aeration are used to enhance the rate of BOD reduction. Older facilities may use aerated lagoons while more recent installations usually use activated sludge in aeration tanks.

A world-class mill with primary and secondary wastewater treatment may produce 100 to 150 tons per day of dry solids in the sludge. This quantity is roughly equivalent to the sludge produced by a municipal treatment plant that services a city of about one million people. In the northeast and midwest regions of the U.S., a number of smaller mills continue to operate. Figure 4 is a size distribution of mills producing primary and secondary sludge in the eleven northeast and midwest states.

Pulp mill sludge have long been thought of as a benign waste with some redeeming features as a fertilizer. As shown in Table 6 (Blosser and Miner, 1986), the industry has been heavily dependent upon land-based disposal methods. Prior to 1980, the cost of sludge disposal by landfilling was a small if not insignificant cost in the overall operation of a pulp mill.

Several years ago, it was discovered that pulp mill sludges and wastewater effluents contain small but measurable concentrations of dioxins (U.S. EPA, 1987). Since that time, pulp mill sludges and wastewaters have received considerable attention by the EPA and state regulatory agencies (U.S. EPA, 1988). In some cases, states have threatened to withhold renewal of discharge permits pending reduction of dioxin emissions.

Dioxin formation in pulp mill effluents has now been traced backed to the bleaching of fibers with chlorine (U.S. Congress, 1989). It has also been found that dioxin formation can be reduced significantly by substituting chlorine dioxide for chlorine as the bleaching chemical. Although chlorine dioxide is significantly more expensive than chlorine, this chemical substitution does not require hardware modifications and is one of the simplest and least expensive methods of reducing dioxin emission. Thus, the dioxin concern may be viewed as a short-term problem in the pulp and paper industry.

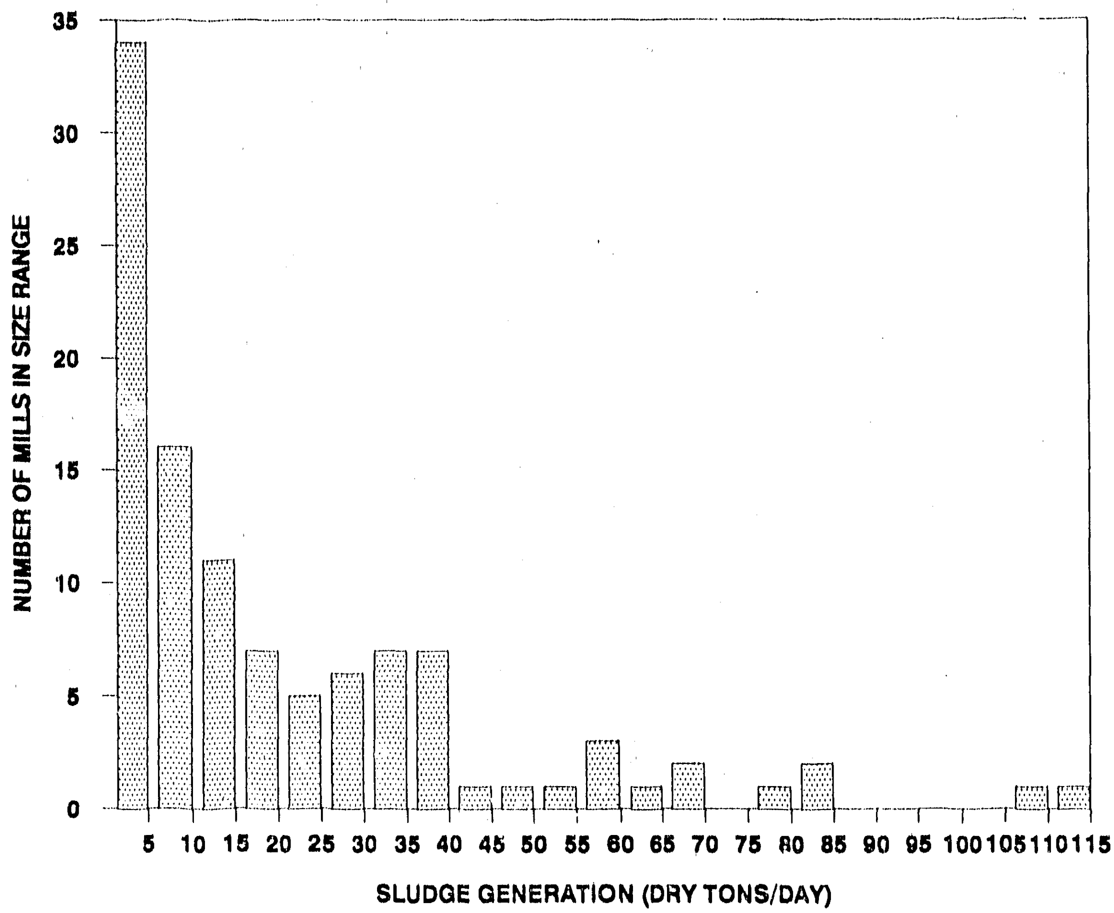


FIGURE 4. PULP MILL SIZE DISTRIBUTION IN THE NORTHEAST AND MIDWEST

Dioxin is only one of many chemicals of potential concern in pulp mill sludges. Bleaching by its very nature involves chemical reactions that can create by-products which are far more hazardous than the starting material. Chlorine bleaching of pulp mill fiber, whether it be by molecular chlorine or chlorine dioxide, will create chlorinated hydrocarbon by-products in much the same manner that chlorination of sewer treatment plant effluent creates chlorinated hydrocarbons (U.S. EPA, 1982). For example, the 'Total Organic Halide' (commonly referred to as TOX) in a pulp mill sludge may range from tens to thousands of parts per million (ppm), depending on the solids content. Some pulp and paper companies have already begun to analyze their effluents for TOX in the realization that it may well become the next focal point for regulatory concern.

TABLE 6. DISPOSAL OF PAPERMILL SLUDGES IN 1975
(from Blosser and Miner, 1986)

Method	Number of Mills	Dry Tons/Day	Percent of Total
Incineration	19	291	10
Landfilled	40	943	33
Landplaced	53	1,118	39
Incineration + Landfilled	4	74	3
Incineration + Landplaced	4	62	2
Recycled	5	28	1
Sold	3	5	--
Lagoon	13	200	7
Municipal/Contractor	3	5	--
Municipal + Landplaced	7	23	1
Municipal + Landfilled	3	10	--
Other	9	87	4
Totals	163	2,846	100

The bottom line is clear: land disposal of pulp mill sludges is becoming more problematic and may cease to be an available option in the not too distant future. Alternative treatment methods that are environmentally acceptable for now and for the foreseeable future would be welcomed by the industry even at a premium price.

MODEC believes that supercritical water oxidation of pulp mill sludges is not only environmentally acceptable, but also cost competitive with landfilling. If it were commercially available today at the projected cost, there is little doubt that it would be the method of choice. MODEC's major objective for the next several years is to scale the SCWO technology to commercially-viable sizes for pulp and paper mill sludge treatment and to demonstrate that such systems can operate safely and reliably with a minimum of operator attention.

IV. SUPERCRITICAL WATER OXIDATION

SCWO is a process for oxidizing organic materials, thereby converting them to carbon dioxide and inorganic acids (see, e.g., Modell, 1988). The overall chemical transformations are analogous to those in incineration, but the way in which the oxidation is conducted is very different. Unlike incineration, SCWO is conducted at mild temperatures (400 to 650°C), where many alloys maintain mechanical strength. Instead of ultrafast reaction in an inherently unstable flame, SCWO takes minutes to complete, but in a stable, plug-flow reactor. The oxidation zone occupies the whole reactor; waste cannot short-circuit or bypass the oxidation zone.

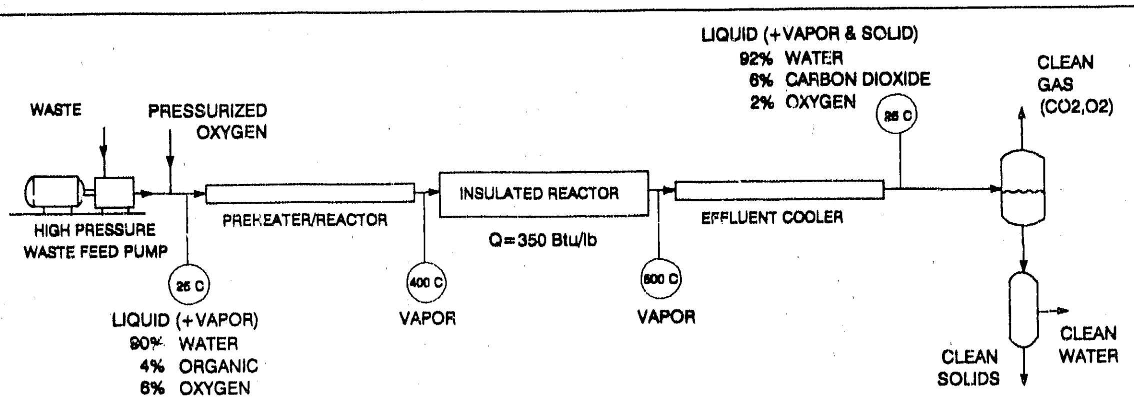
At atmospheric pressure, it is not possible to oxidize organics at 400 to 650°C. Before they oxidize, organics usually char, and char burns effectively only at high temperature. Oxidation at the mild temperatures of SCWO conditions is made possible by high pressure and the presence of water as the reaction medium. Water above 374°C and 218 atm (3200 psi) is a supercritical fluid. In that state, supercritical water (SCW) becomes a superb solvent for organic materials as well as gases. In addition, SCW reacts with organics and reforms them to small molecules - without the formation of char (Modell, 1985(1)). These small molecules are readily oxidized if air or oxygen is mixed with the organic-SCW mixture.

A. Basic Phenomena in SCWO

A schematic of the heat exchangers and reactors of an SCWO system is shown in Figure 5, along with examples of chemical transformations. The essential features are as follows:

1. Sludge is pressurized to the operating pressure of 250 atm (3700 psi). Oxygen, supplied as a cryogenic liquid, is also pressurized, heated to room temperature and mixed with the waste. At this point, the mixture of waste and oxygen consists of two phases, liquid (waste) and vapor (oxygen), in a weight ratio of about 94% waste and 6% oxygen.

2. The mixture of waste and oxygen, at room temperature and operating pressure, enters the preheater/reactor, where it is heated to a temperature ranging from 300 to 400°C, depending on the concentration of oxidizable material in the waste. The oxidation begins in the preheater.



HYDROCARBONS	C6H6 + 7.5 O2 Benzene	=	6 CO2 + 3 H2O
ORGANIC CHLORIDES	Cl2-C6H2-O2-C6H2-Cl2 + 11 O2 Dioxin	=	12 CO2 + 4 HCl
	CHCl3 + 0.5 O2 + H2O Chloroform	=	CO2 + 3 HCl
ORGANIC SULFIDES	Cl-C2H4-S-C2H4-Cl + 7 O2 HD	=	4 CO2 + 2 H2O + 2 HCl + H2SO4
ORGANIC NITROGEN	CH3-C6H2-(NO2)3 + 5.25 O2 TNT	=	7 CO2 + 2.5 H2O + 1.5 N2
HEAVY METALS	Pu(NO3)4 + 2 H2O + 2 CO2 Radioactive wastes	=	Pu(CO3)2 + 4 HNO3

FIGURE 5. THE CHEMISTRY OF SUPERCRITICAL WATER OXIDATION

3. The example in Figure 5 shows the waste being heated to 400°C. Somewhere in the range of 360 to 380°C, it is thought that the liquid phase disappears. The only remaining fluid phase is a vapor, in which the organic and oxygen are intimately mixed. From the preheater, the reacting mixture enters an insulated reactor, where most of the remaining organic is oxidized. It is within this reactor that the maximum temperature is reached. To attain very high destruction efficiencies, peak temperatures in the range of 600°C are desirable.

   The peak temperature in the reactor is determined by (i) the amount of heating done in the preheater/reactor and (ii) the heating value of the waste mixture. The more preheating, the less heating value required to reach a given outlet temperature. The example shown in Figure 5 is representative of the conditions required to destroy a very dilute waste, with a heating value of the order of 350 Btu/lb (5 wt-% sludge). For such a waste, the preheater exit temperature might be around 400°C.

4. After leaving the insulated reactor, the mixture is cooled in a heat exchanger back to room temperature. As the effluent proceeds down the heat exchanger, water vapor condenses and forms a liquid which eventually becomes the continuous phase. This liquid dissolves acid gases (i.e., hydrochloric, sulfuric and phosphoric acids) and traps particulates. The residual gas phase is primarily excess oxygen and carbon dioxide.

5. The effluent is separated into gas, liquid and solid phases. The liquid and solid effluents are depressurized; the gas phase is processed to separate oxygen from carbon dioxide. The former is recycled back to the process. The carbon dioxide can be liquefied, stored as a liquid, and sold back to the oxygen supplier.

The chemical reactions shown in Figure 5 illustrate the types of products formed during SCWO of hazardous materials. Benzene, like all hydrocarbons, forms only carbon dioxide and water. Organic chlorides, including heavy compounds like dioxin and pesticides as well as light compounds like volatile organic halides, form hydrochloric acid. Organic sulfides, including chemical agents like mustard gas HD form sulfuric acid.

Organic nitrogen is a special case. Modell and coworkers have shown that organic nitrogen compounds do not form NO_x (i.e., NO or NO_2) during SCWO. Below 500°C, ammonia is the primary nitrogen-containing product; above 600°C, molecular nitrogen (N_2) and nitrous oxide (N_2O) are formed (Timberlake et al., 1982).

Recently, Modell Development has invented a method of treating mixed rad wastes (mixtures of organics, inorganics and radioactive nuclides in water) during tests con-ducted at Sandia National Laboratory in Livermore, California. The details are being kept as proprietary until patentability can be established.

Over the past six years, destruction efficiencies for a number of hazardous organic chemicals have been reported. Table 7 is a listing of some results pertinent to this project. With one exception, the destruction efficiencies (DE's) reported in Table 7 are measured by the degree of removal of *all* organic matter from feed to aqueous effluent. The destruction/reduction efficiency (DRE) reported for dioxin is the less stringent parameter, used by EPA, which measures only the reduction of dioxin from influent to effluent.

TABLE 7. DESTRUCTION EFFICIENCIES OF HAZARDOUS ORGANICS BY SUPERCRITICAL WATER OXIDATION

Class /Compound	Temperature (°C)	Residence Time (min)	Destruction Efficiency (%)	Reference
Organic Nitro Compounds				
2,4-Dinitrotoluene	457	0.5	99.7	Thomason, 1984
2,4-Dinitrotoluene	513	0.5	99.992	Thomason, 1984
2,4-Dinitrotoluene	574	0.5	99.9998	Thomason, 1984
Halogenated Aliphatics				
1,1,1-Trichloroethane	495	3.6	99.99	Modell, 1985 (2)
1,2-Ethylene dichloride	495	3.6	99.99	Modell, 1985 (2)
1,1,2,2-tetrachloroethylene	495	3.6	99.99	Modell, 1985 (2)
Halogenated Aromatics				
Hexachlorocyclopentadiene	488	3.5	99.99	Modell, 1985 (2)
o-chlorotoluene	495	3.6	99.99	Modell, 1985 (2)
1,2,4 Trichlorobenzene	495	3.6	99.99	Modell, 1985 (2)
4,4-Dichlorobiphenyl	500	4.4	99.993	Modell, 1985 (2)
DDT	505	3.7	99.997	Modell, 1985 (2)
PCB 1234	510	3.7	99.99	Modell, 1985 (2)
PCB 1254	510	3.7	99.99	Modell, 1985 (2)
Dioxin (2,3,7,8-TCDD)	574	3.7	99.99995*	

* Destruction/reduction efficiency, DRE

The 2,4-dinitrotoluene results show the dramatic effect of increasing temperature: the DE increases from nearly three 9's to nearly six 9's in going from 457 to 574°C. Table 7 also shows that chlorinated aromatics can be destroyed readily - to four 9's at a relatively mild 500°C. MODEC has recently measured the DRE of 2,3,7,8-TCDD (dioxin) at 574°C and has found better than six 9's at 3.7 minutes residence time. It should also be noted that volatile organic chlorides are also readily destroyed.

B. Modell Development's SCWO Process

A simplified schematic of a SCWO system that MODEC has designed for treating sludges is shown in Figure 6. Waste is pumped from a feed tank to operating pressure (3700 psi). Liquid oxygen would be stored on site in a cryogenic tank and fed, as needed, through a cryogenic pump and evaporator. The pressurized mixture of waste and oxygen are passed through the preheater/ reactor, insulated reactor, and effluent cooler. Prior to 1989, SCWO technology was limited to processing wastes without inorganics because salts would precipitate out in the reactors and clog them (Modell, 1988). Over the past two years, MODEC has devised proprietary designs for these components which allow processing wastes containing inorganic salts and solids - without clogging components.

The effluent from the cooler is a mixture of vapor (excess oxygen and carbon dioxide), liquid (water, carbon dioxide, inorganic salts and acids), and perhaps solids (metal oxides and carbonates, silica, alumina, or other inerts that may have been present in the feed and were not soluble in the aqueous effluent). Each of these phases is separated and then depressurized. (The solid-liquid separation is a new method perfected by MODEC.)

In treating sludges, cost-effectiveness is extremely important because SCWO is competing with landfilling and incineration. MODEC's SCWO process is cost-effective for treating dilute aqueous wastes because it uses regenerative heat exchange to heat the feed and cool the effluent. As shown in Figure 6, an external heat transfer loop is used. Fluid circulating within this loop picks up heat in the effluent cooler and passes it to the preheater/reactor. In this manner, wastes with as little as 350 Btu/lb can be treated without requiring auxiliary fuel.

C. Stability and Control of the SCWO Process

Because SCWO is a new technology and because it addresses treatment of hazardous wastes, questions of stability and control are of concern to prospective users of the technology.

There are two extremely important safety features of the SCWO process that should be noted here. *The oxidation reaction temperature cannot run away* (i.e., the temperature cannot increase to a dangerous level where, for example, the reactor might lose its strength and burst or melt down). The maximum temperature possible is the peak temperature reached when waste is completely oxidized; that temperature is set by the degree of preheating and the concentration of waste. Secondly, *the reactor does not contain an explosive mixture*. The presence of a high concentration of water dilutes and moderates the mixture below the limit required

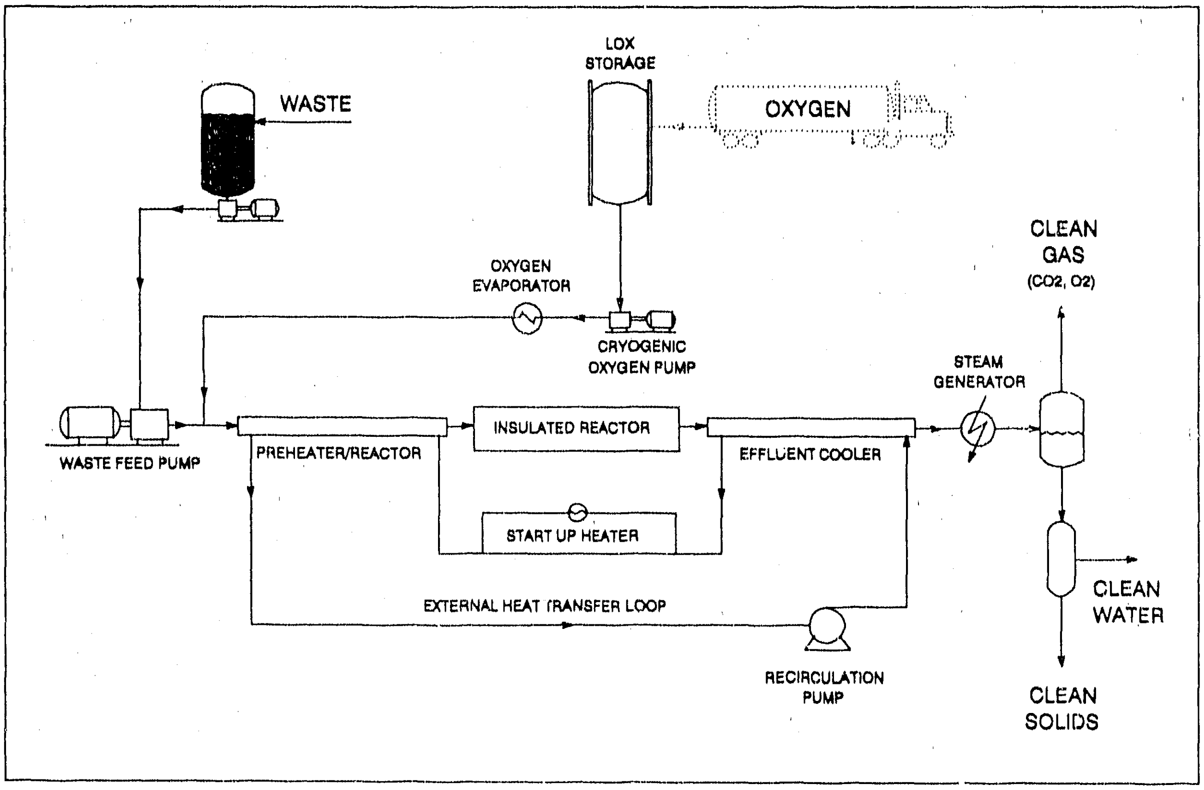


FIGURE 6. SCHEMATIC OF A SCWO SYSTEM FOR WASTE DESTRUCTION

for explosive combustion. Furthermore, because the waste is fed as a mixture in water, there is no way for the organic to reach the reactor without the moderating effects of the carrier water.

The control of a SCWO system is rather straight-forward. In essence, there are five feed-back control loops that maintain steady-state conditions: (1) the waste feed rate is controlled by feedback from a flow meter to the high pressure feed pump motor (or stroke length adjuster); (2) the oxygen flow rate is controlled by feedback from an oxygen concentration monitor in the gaseous effluent line; (3) the reactor temperature is controlled by the external heating loop fluid flowrate; (4) the system pressure is controlled by a flow control loop on the gaseous effluent line; and (5) the liquid level in the gas/liquid-solid separator is controlled by a flow control loop on the effluent liquid line.

Startup and shutdown have also been perfected and are now straight-forward procedures. During startup, the system is pressurized with clean water and oxygen, the flow rates of which are set to the range desired during waste treatment. A startup heater on the external heat transfer loop is energized, and the preheater/reactor is brought to operating temperature by recirculation of the external fluid. (MODEC has perfected a rapid, non-flame method for startup, using direct ohmic heating of the external loop lines with low voltage AC.) When the preheater exit temperature has exceeded 300°C, the liquid feed is switched from clean water to a mixture of water and organic (e.g., 2 wt-% organic fuel in water). The organic is oxidized in the reactor. The heat liberated rapidly brings the reactor to temperature and the hot effluent, in turn, heats the external loop fluid in the effluent cooler. In this manner, the system is brought to thermal steady-state in a highly reliable way prior to the introduction of waste. Once at this condition, the liquid feed can be switched from organic-water to waste without any thermal transients. Thus, a steady and high destruction efficiency can be assured from the moment waste is introduced.

For shutdown, the procedure can be reversed (i.e., waste -> organic + water -> water) so as to purge the system of all waste prior to cooling the system with clean water and oxygen. If emergency shutdown is required, feed and oxygen flow are immediately shut off. The system is bottled up tightly by closing isolation valves on all inlet and outlet lines. The system will then cool slowly (or rapidly, if desired, by switching the external heat transfer fluid to cold water) and the pressure will fall as the vapor in the system condenses.

V. SCWO BENCH SCALE TESTS

The objective of these tests was to determine if SCWO can effectively oxidize the organic matter in pulp mill sludges, including dioxin constituents. Specifically, the objective was to determine the destruction efficiencies of total organic carbon and 2,3,7,8,-TCDD (dioxin), in the SCWO temperature range of 400 to 600°C, using actual sludges from pulp mills.

MODEC has a bench scale SCWO system that has been used to demonstrate destruction of secondary sludges from municipal sewage treatment. MODEC proposed to the DOE Office of Industrial Programs (OIP) that MODEC obtain an anonymous sample of sludge through the National Council on Air and Stream Improvement (NCASI), an industry-supported non-profit organization. NCASI has been conducting dioxin tests for the pulp and paper industry and agreed to provide MODEC with a sludge sample from an actual mill. After initiating this project, MODEC received permission from a pulp and paper company to publish some results from a second test of actual pulp mill sludge. Both sets of results are reported herein.

The sludge samples were mixtures of primary and secondary sludge. The feed sludge and the aqueous and solid effluents from the SCWO test were analyzed for organic carbon, 2,3,7,8- TCDD and 2,3,7,8-TCDF, total organic halide (TOX) and inorganic elements.

In order to establish the destruction efficiency of dioxin, a run was also made with an aqueous solution of 0.5 ppm of 2,3,7,8-TCDD. Methyl ethyl ketone was added to provide a background of oxidation in which to measure TCDD destruction/reduction efficiency (DRE).

A. MODEC's Bench System

MODEC has designed and constructed a bench scale SCWO unit, shown schematically in Figure 7. This third-generation unit is used to perform waste tests and to obtain design data. It is a prototype of MODEC's commercial system, simulating the time-temperature history that a waste would experience in a commercial scale system. It is capable of processing an aqueous feed of up to 80 cc/min (30 GPD), containing up to 3,000 Btu/lb with up to 10 wt-% solids of particles smaller than 100 micron. Reactor operating limits for pulp mill sludge are presently 600°C and 3700 psi. Residence times can range from 10 seconds to 10 minutes.

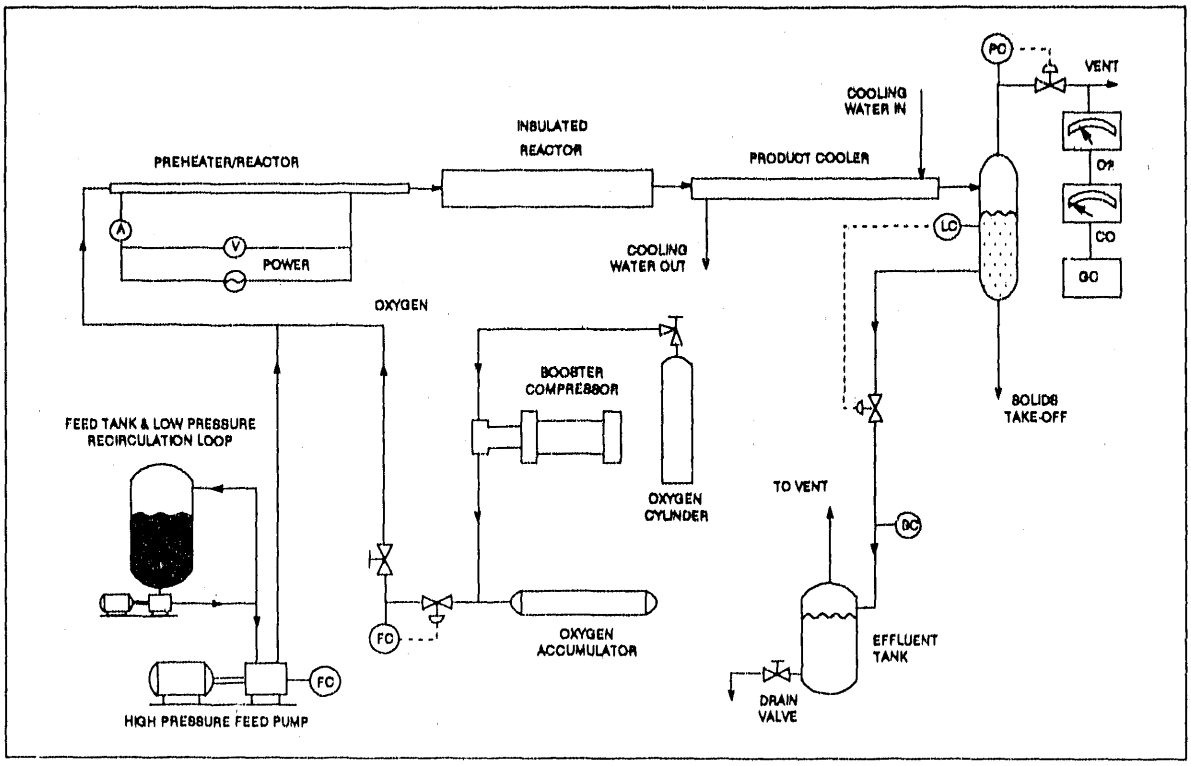


FIGURE 7. BENCH SCALE SCWO SYSTEM

With reference to Figure 7, the feed is recirculated through a low pressure loop to keep it well-mixed. A small portion of flow is fed to a pump which pressurizes the sludge to 3700 psi. Oxygen is pressurized from cylinders by a booster to an accumulator, fed through a metered flow-control loop, and mixed with the sludge. The sludge/oxygen mixture is heated to the desired oxidation temperature by direct ohmic heating of the preheater/reactor. The mixture then passes to an insulated reactor, where the temperature increases due to the heat released by oxidation.

The reactor effluent is cooled to room temperature and fed to a solid-liquid-gas separator. Effluent gas flow rate is controlled to maintain the desired operating pressure, while liquid take-off is controlled to maintain a constant liquid level. Inorganic solids are removed through a proprietary arrangement. The vent gases are analyzed for oxygen and carbon monoxide by on-line analyzers and for carbon dioxide and volatile hydrocarbons by gas chromatography with dual thermal conductivity and flame ionization detectors. Liquid and solid samples are sent to outside laboratories for analyses.

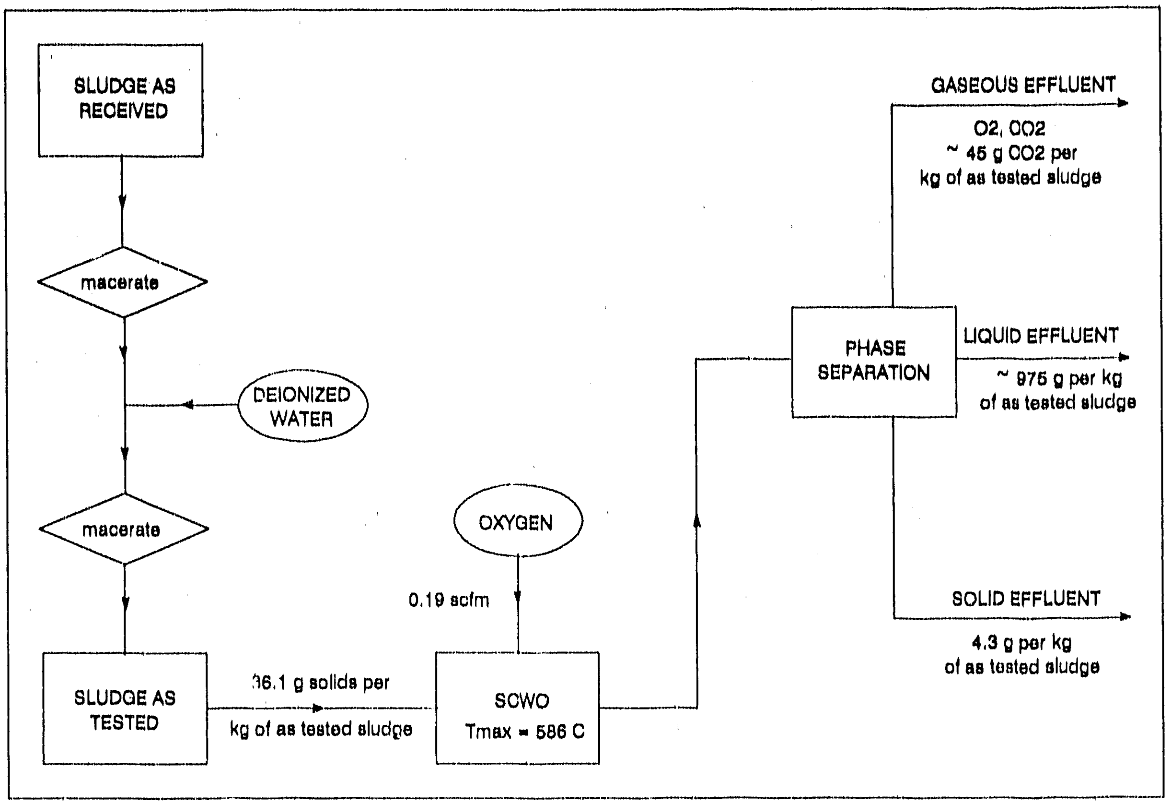


FIGURE 8. SLUDGE PREPARATION AND MASS BALANCE

B. FEED PREPARATION

The high pressure feed pump in the MODEC bench scale system is limited to slurries with particle size under 100 micron. (Pumps for commercial scale systems can accept particles of up to 2 mm.) Samples with particles larger than 100 micron were pretreated using a bench scale in-line wet macerator and/or a laboratory-scale homogenizer.

NCASI submitted a sludge sample from an unknown facility in January 1990. The raw sludge was determined to have 7.2 wt-% solids. With reference to Figure 8, the sludge was macerated using the coarse and medium heads of the bench scale macerator. The sludge was diluted to about 4 wt-%, and a pumping test was performed. The pump discharge flow was slightly erratic, so the sludge was again diluted to 3.7 wt-% and again macerated with a fine head on the macerator and homogenized. The resulting material could be readily pumped by the high pressure feed pump. As shown in Figure 8, the 'as tested' material was used as the starting material for subsequent SCWO tests.

TABLE 8. SCWO RUN CONDITIONS

Run No.	Feed	Date	Duration (hr)	Feed Flowrate (cc/min)	Oxygen Flowrate (SCFM)	Peak Reactor Temperature (°C)
1	Sludge	1/22/90	5.25	69	0.19	590
2	Sludge	1/25/90	6.8	71	0.19	574
3	Dioxin	2/01/90	2.3	52	0.19	574

Due to the high cost of 2,3,7,8-TCDD, MODEC conducted only one test with the pure material. The dioxin was dissolved in a solvent containing 1.9 wt-% methyl ethyl ketone (MEK), the balance being deionized water. The feed solution contained 0.5 ppm of the 2,3,7,8-TCDD.

C. Results and Discussion

1. **Run Conditions.** A total of two runs were made using the pulp mill sludge. The conditions are shown in the Table 8. In runs 1 and 2, some fluctuations in feed flow rate were noticed, but the runs were completed without interruption. Mr. David Buckley of NCASI witnessed run 2. Run 3, with a feed of 2,3,7,8- TCDD in MEK, was uneventful and conditions were steady throughout.

2. **Analytical Results.** The analyses of 'as tested' sludge, aqueous effluent and solid effluent are given in Table 9 for both the sludges obtained from NCASI and from a pulp and paper company. The concentrations of total solids and elements are in mg/kg of sludge (i.e., wet basis), which is equivalent to parts per million by weight (ppm). The TCDD and TCDF concentrations are in picograms per gram of sludge (wet basis), which is parts per trillion (ppt).

   The sludges were 3.6 and 4.4 wt-% solids, respectively. The analyses for major, minor, and trace elements are presented on a dry basis. The organic content, represented by three major elements (CHO), accounts for about 70% of the weight of the sludge solids. The 12 minor elements account for an additional 5% and the 13 trace elements for about 0.5%. The remaining 25% must be distributed amongst the roughly 80 elements for which analyses were not requested.

TABLE 9. SCWO BENCH SCALE TESTS RESULTS

	CONCENTRATION (mg/kg unless otherwise noted)							
	NCASI, 567 °C				Company X, 586 °C			
ANALYTICAL TEST	Sludge	Aqueous	Solids	Destruction (%)	Sludge	Aqueous	Solids	Destruction (%)
Total solids	36,100	NA	4,300	88	43,900	NA	8,900	80
2, 3, 7, 8-TCDD (pg/g)	0.34	0.0031	1.9	96.7	123	ND(.02)	2.9	99.98
2, 3, 7, 8-TCDF (pg/g)	1.58	ND(.0027)	5.3	>98.4	834	ND(.01)	25.6	99.97
MAJOR ELEMENTS								
Carbon	12,043	27	18,500	99.1	16,362	16	11,000	99.3
Oxygen	11,545	NA	51,800	98.1	13,109	NA	35,600	97.6
Hydrogen	1,563	NA	10,250	97.2	1,664	NA	5,300	97.2
CHO - SUBTOTALS	25,151	27	80,550	98.5	31,134	16	51,900	98.5
	Sludge	Aqueous	Solids	Recovery (%)	Sludge	Aqueous	Solids	Recovery (%)
MINOR ELEMENTS								
Aluminum	132	5	63,600	211	281	7	36,100	117
Calcium	678	256	29,500	55	474	460	8,380	109
Chlorine	329	186	246	55	208	210	125	97
Iron	25	ND	3,590	61	229	0	18,000	70
Magnesium	40	1	3,240	37	32	3	2,320	74
Manganese	20	1	1,440	34	6	0	355	66
Nitrogen	217	167	148	84	145	18	187	13
Phosphorus	17	1	10	8	25	1	186	10
Potassium	ND	8.7	2,270		ND	12	1,900	
Silicon	40	73	196	181	74	160	867	218
Sodium	146	103	9,960	97	68	77	2,090	137
Sulphur	159	105	0	64	417	413	2	95
MINOR - SUBTOTALS	1,803	927	114,199	77	1,958	1,363	70,512	99
Distribution		50%	27%			67%	32%	
TRACE ELEMENTS								
Arsenic	ND	0.008	ND		0.24	0.019	37	145
Barium	2	0.21	147	44	ND	0.06	210	
Boron	ND	0.31	1.6		ND	0.22	1.4	
Cadmium	ND	ND	0.4		ND	0.01	1.0	
Chromium	1.0	0.89	206	177	4.5	0.11	355	73
Copper	1.4	0.06	59	22	1.6	0.39	100	79
Lead	ND	ND	20		ND	ND	27	
Mercury	ND	ND	0.60		0.01	0.0023	0.70	84
Nickel	1.8	0.05	182	46	2.3	0.40	410	175
Selenium	ND	ND	ND		ND	0.01	1.9	
Silver	ND	ND	1.1		0.08	ND	2.1	23
Strontium	1.0	0.31	62	57	0.9	0.90	40	136
Zinc	5.8	0.26	296	26	7.2	0.55	488	68
TRACE - SUBTOTALS	13	2	975	48	17	3	1,674	104
Distribution		16%	33%			15%	89%	

Of the three products (gaseous, aqueous and solid effluents), the gaseous effluent was the least interesting. The gas chromatographic analyses yielded primarily oxygen and carbon dioxide, with small concentrations of nitrogen.

The analyses for elements in the aqueous and solid effluent are presented in Table 9 on the basis of mg element per kg of aqueous effluent, which is ppm by weight. The amounts of aqueous and solid effluents obtained from a kg of wet sludge were measured (see, e.g.,Figure 8 for the sludge obtained from NCASI). Given those relative weights and concentrations of elements, it is possible to calculate destruction efficiencies for the CHO elements and recovery efficiencies for all of the other elements. The destruction efficiencies are discussed in a subsequent subsection.

The recovery efficiencies of minor elements give some measure of the degree of accuracy of the analytical results. The overall recoveries of 77 and 99% for the two sludges indicate that solids recovery in the SCWO bench system is high and the analytical measurements average out to the right order of magnitude. For individual elements, recovery efficiencies above 100% can be attributed to inaccuracies in the measurement of the element concentration in the sludge.

3. **TOC Destruction Efficiencies.** The total organic carbon (TOC) of a sludge is difficult to measure accurately. Past experience indicated that: (i) sludge sampling is very difficult to do uniformly, and (ii) conventional TOC instruments, using ultraviolet (UV) and chemical oxidizer do not provide accurate measurements. MODEC has found the most meaningful measure of influent TOC to be the carbon content of the sludge solids, as measured-by-percent by weight of carbon from a sample of sludge dried in an evacuated dessicator.

   Both sludge solids and solid effluent were analyzed for carbon content and carbonate carbon, the difference usually being attributed to organic carbon. For both sludge samples tested, the carbonate carbon were negligible in feed and effluent solids. Thus, TOC destruction efficiency was calculated as shown in Figure 9 for the sludge obtained from NCASI. The results for the two sludges (given in Table 9 under carbon destruction) were 99.1% and 99.3%. These values are lower by one to three 9's than those reported for single compounds under similar

FIGURE 9. TOC DESTRUCTION EFFICIENCY
(basis: 1 L of sludge, as tested)

In feed, @ 12,043	=	12,043 mg
In aqueous effluent, @ 27 ppm	=	27 mg
In solid effluent, @ 18,558 ppm x .0043 g/g	=	84.17 mg
Residual	=	107 mg
Residual, % of feed (107/12,043)	=	0.89%
Destruction efficiency	=	99.1%

conditions (e.g., see Table 7). However, 99% destruction efficiencies for TOC in sludges is considered to be an excellent result.

4. **TOX Destruction Efficiency.** The total organic halide (TOX) values, reported in Figure 10, consisted of a combination of measurements. The sludge feed was separated into a concentrate and a supernate. The concentrate, containing the bulk of the organic halide, was analyzed for total halide, TX, and inorganic halide, IX. The TOX was calculated by difference (TOX=TX-IX). The supernate was analyzed for adsorbable organic halide, AOX; its contribution to the total was about 5%. The organic halide content of the effluents was determined by AOX in the aqueous phase and extractable organic halide (EOX) in the solid phase. The error bands of ±50% are conservative guestimates made by MODEC to reflect the fact that the measured values of AOX and EOX were close to their detectable limits.

   Based on the analytical results shown in Figure 10, TOX destruction efficiency was calculated to be 99.94% (see Figure 11). This value is an order of magnitude higher than the 99% TOC destruction efficiency. In general, organic chlorides tend to have higher destruction efficiencies than hydrocarbons, possibly because the C-Cl bond is usually weaker than the C-H bond.

5. **TCDD and TCDF Destruction/Reduction Efficiencies.** The calculations for the TCDD and TCDF destruction/reduction efficiencies (DRE's) are shown in Figure 12 for the sludge obtained by NCASI. Note that since the analyses are for specific chemicals, the result is expressed as destruction/reduction rather than simply destruction efficiency.

FIGURE 10. ORGANIC HALIDE ANALYSES

	Weight %	Density (g/mL)	AOX (mg/L)	IX (mg/L)	IX (mg/kg)	TX (mg/kg)	EOX (mg/kg)	TOX (mg/kg)	TOX (mg/L)	TOX + AOX (in 1 L of feed)	
In feed											
Liquid	96.7		5	163						4.8 mg	
Solids	3.3	1.02			1300	5200		3900	3978	131.3 mg	
									Total	136.1 mg	
In effluent											
Aqueous			0.006	186						0.006 mg	±50%
Solids	99.2				44	246	16.9			0.072 mg	±50%
									Total	0.078 mg	±50%

In general, one would expect the DRE for chlorinated compounds TCDD and TCDF to be higher than the TOX destruction efficiency. This is not the case for the sludge obtained for us by NCASI. The DRE's of 96.7% and 98.4% are one to two orders of magnitude lower than the 99.94% value for TOX. (Compare the residuals, as percent of feed, in Figures 12 and 11.)

MODEC believes that these results underscore the efficiency of SCWO for dioxin destruction because the feed sludge contained unexpectedly low TCDD and TCDF concentrations. The levels of 0.34 and 1.58 pg/g in the sludge are considerably lower (by 1 to 2 orders of magnitude) than that anticipated by NCASI. Samples from the same mill had much higher concentrations last year and the mill had not changed its process in the interim. Due to the extraordinary time lag in getting dioxin analyses done (3 months), MODEC did not learn of the low concentrations until the project was near completion.

In Table 9, the DRE's for TCDD and TCDF are shown for the two

FIGURE 11. TOX DESTRUCTION EFFICIENCY
(basis: 1 L of sludge, as tested)

In feed, @ 136.1 mg/kg	=	136.1 mg
In aqueous effluent, @ AOX of 0.006 mg/L	=	0.006 mg
In solid effluent, @ EOX of 16.9 mg/kg x .0043 g/g	=	0.072 mg
Residual	=	0.078 mg
Residual, % of feed	=	0.057%
Destruction efficiency	=	99.94%

sludges that were tested. Note that the DRE's exceeded 99.97% for the sludge obtained from Company X. Those DRE's are consistent with TOX reduction efficiency of 99.94%. The difference between the two sludges is the magnitude of the TCDD and TCDF concentrations in the feed.

The results of the test conducted with the 2,3,7,8-TCDD solution confirm the above interpretation and demonstrate the ability of SCWO to destroy dioxin. The results for TCDD and TOC are shown in Figure 13. The feed contained 0.5 ppm TCDD and 1.9 wt-% methyl ethyl ketone in water. The TCDD concentration in the effluent of 264 pg/liter is equivalent to a DRE of more than 99.9999% (six 9's). The TOC reduction of about 99.9% is also consistent with the values obtained for the two sludges.

FIGURE 12. TCDD AND TCDF DESTRUCTION EFFICIENCIES FOR NCASI SLUDGE (basis: 1 L of sludge, as tested)

2, 3, 7, 8 -TCDD	=	
In feed, @ 0.34 pg/g*	=	340 pg
In aqueous effluent, @ 0.0031 pg/g	=	3.1 pg
In solid effluent, @ 1.9 pg/g x .0043 g/g	=	8.2 pg
Residual	=	11.3%
Residual, % of feed = (11/340)*100	=	3.3%
Destruction/reduction efficiency	=	96.7%
2, 3, 7, 8 -TCDF		
In feed, @ 1.58 pg/g	=	1,580 pg
In aqueous effluent, @ detection limit of 0.0027 pg/g	=	2.7 pg
In solid effluent, @ 5.3 pg/g x .0043 g/g	=	22.8 pg
Maximum possible residual	=	25.5 pg
Residual, % of feed = (25/1580)*100	=	1.6%
Minimum possible destruction/reduction efficiency	=	98.40%

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*picograms/grams

FIGURE 13. TCDD AND TOC DESTRUCTION EFFICIENCIES FOR DIOXIN SOLUTION
(basis: 1 L of dioxin feed, as tested)

2, 3, 7, 8 -TCDD	=	
In feed, @ 0.5 mg /L	=	500,000,000 pg
In aqueous effluent, @ 264/pg liter	=	264 pg
Residual, % of feed = $(264/5 \times 10^8)*100$	=	0.00005%
TCDD destruction/reduction efficiency	=	99.99995%
TOC		
In feed, @ 14,100 ppm	=	14,100 ppm
In aqueous effluent, @ 18.1 ppm	=	18 ppm
Residual, % of feed residual + (18.1/14,100)*100	=	0.13%
TOC destruction efficiency	=	99.87%

In summary, we view the destruction efficiency results very favorably. If necessary, higher DRE's could probably be achieved by increasing temperature and/or increasing residence time. Alternatively, the solid effluent could be readily washed with an organic solvent to remove any residual traces, and the spent organic solvent mixed with the sludge feed for destruction.

6. **Disposition of the Solid Effluent.** Samples of the solid effluent were submitted for analysis by the EPA TCLP test. In essence, the solids are leached with mild acids and the extract is analyzed for pollutants that might be leached out by, e.g., acidic rainwater.

The results of the TCLP tests are given in Table 10, along with EPA's groundwater pollution criteria. Benzene and lead were the only pollutants with measured concentration above the groundwater limit. (Benzo(a)pyrene and PCB had detection limits above the groundwater limit.) The 80 parts per billion (ppb) reported for lead is suspect; lead concentrations have been non-detectable (i.e., below 50 ppb) in TCLP tests of solids from SCWO treatment of other pulp mill sludges. Benzene concentrations of 100 to 400 ppb are consistent with other results. In general, the TCLP results are highly favorable because the groundwater limits are fairly stringent. Based on results such as these,

TABLE 10. COMPARISON OF SOLID EFFLUENT LEACHATE RESULTS WITH EPA'S GROUNDWATER POLLUTION CRITERIA (concentrations in micrograms per liter)

Pollutant	Groundwater Concentration	Solid Effluent TCLP Leachate Results
Arsenic	50.	< 5.
Benzene	5.0	370.
Benzo(a)pyrene	0.3	< 2.5
Bis(2-ethylhexyl)phthalate	248.	25.
Cadmium	10.0	10.
Chlordane	2.1	< 0.25
Copper	1,300.	140.
DDT/DDE/DDD (total)	10.2	< 7.5
Lead	50.	80.
Lindane	4.0	< 0.25
Mercury	2.0	< .5
Nickel	1,750.	< 50.
Polychlorinated biphenyls	0.45	< 2.5
Toxaphene	5.0	< 0.25
Trichloroethane	5.0	< 1.9

the solid effluent could undoubtedly pass the most stringent tests for disposal in sanitary landfills.

7. **Disposition of the Aqueous Effluent.** As shown in Table 9, the aqueous effluent is very clean and undoubtedly reusable. The TOC of 27 ppm is in the range of concentrations found in many urban tap waters around the U.S. The major inorganic species are calcium, chlorine (as chloride ion), nitrogen (as ammonia), sodium and sulfur (as sulfate). The total of the major elements is in the range of 0.1 wt-%. The minor elements are all below EPA's groundwater pollution criteria (see Table 10). Thus, the aqueous effluent could be used within a pulp mill where a high quality of water is needed.

VI. PROCESS DESIGN AND ECONOMICS

In this section, the MODEC process for SCWO treatment of pulp mill sludges is described. Capital and operating cost estimates for full scale SCWO systems at throughputs ranging from 5 to 100 ton/day are presented. An economic comparison is provided of SCWO, incineration, and landfilling for a mill producing 100 ton/day of sludge (dry solids basis).

A. PROCESS DESCRIPTION

A flowsheet for MODEC's SCWO process for pulp mill sludge is shown in Figure 14. It is designed to process a sludge with 10 wt-% solids (primary or secondary or mixed), containing anywhere from 50:50 to 80:20 ratio of organic-to-inorganic components. The process produces clean effluents: a gas which is primarily carbon dioxide (95 to 99.95% CO_2, the balance being O_2, with small amounts of N_2), a liquid which is clean water with some dissolved alkali salts, and a solid which is primarily oxides and insoluble salts of metals contained in the sludge.

The process shown in Figure 14 is particularly well-suited to pulp mill sludge because it can recover about half of the heating value of the sludge as steam without requiring the addition of fuel. In addition, recovery of CO_2 and sale of this by-product to a gas processor can provide a significant credit. Liquefaction of the CO_2 also provides a major environmental benefit that cannot be matched by incineration: the gaseous effluent (i.e., CO_2) can be stored as a liquid and analyzed prior to discharge, thereby preventing uncontrolled or accidental release of any contaminants to the atmosphere.

With reference to Figure 14, the feed sludge is homogenized and recirculated in a low pressure (100 psi) loop. A portion of that mixture is combined with pressurized oxygen and fed to the preheater, then to the reactor and on to the cooldown exchanger. The energy for preheat is obtained by circulating the fluid in the external heat transfer loop. This loop provides the regenerative heat exchange, which eliminates the need for auxiliary fuel. Enough energy is extracted from the effluent in the cooldown exchanger to provide the energy required to preheat the feed and to compensate for heat losses in the external loop. Because there is no net loss or gain of energy by the process fluid in traversing the combination of preheater-reactor-cooldown exchanger, the fluid leaving the cooldown exchanger contains the heating value of the original waste feed, but in the form of thermal energy. From this stream, steam is produced for use external to the SCWO process, thereby reducing prime energy consumption in the pulp mill.

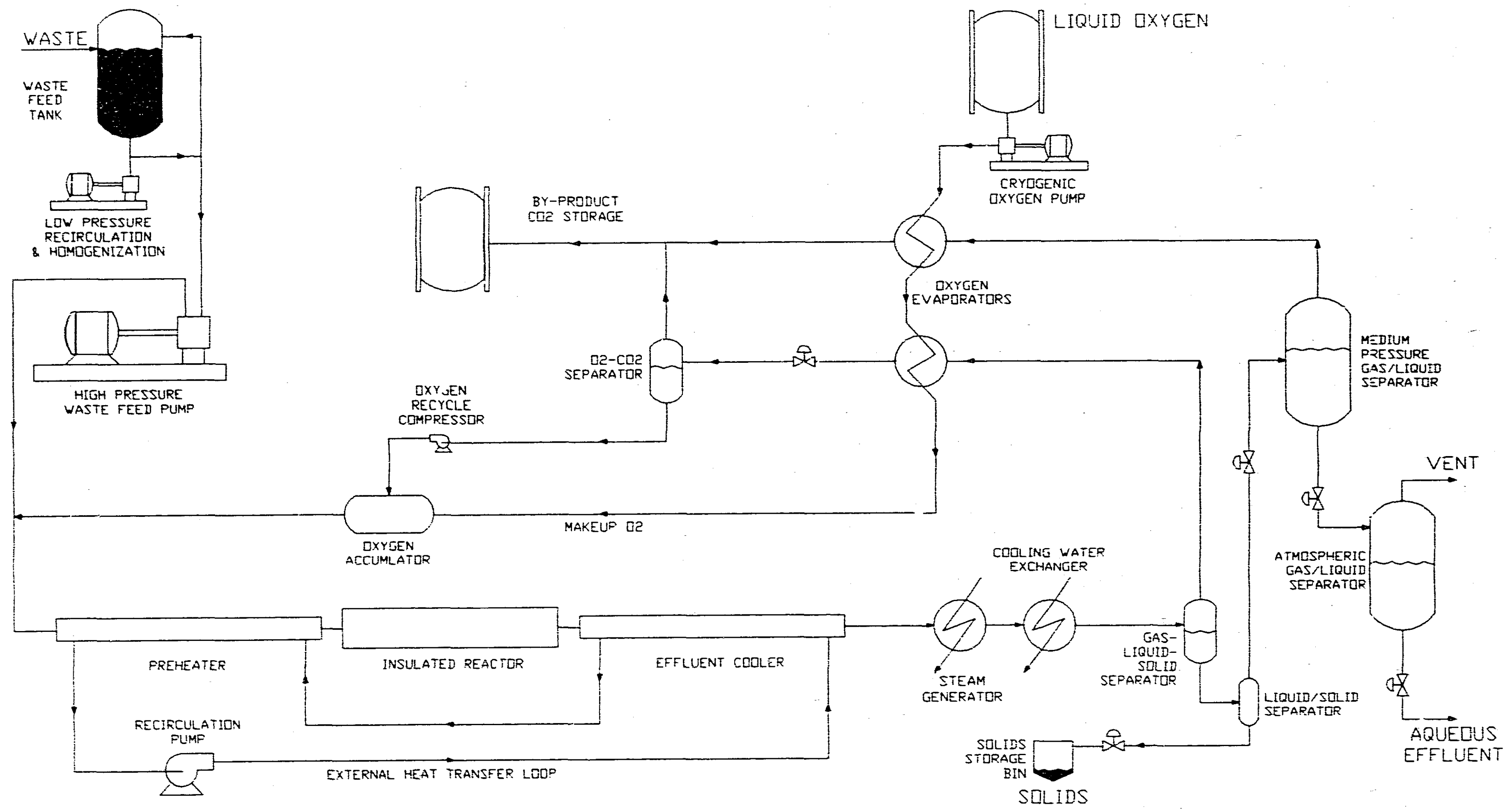

FIGURE 14. MODEC'S PROCESS FOR SCWO TREATMENT OF PULP MILL SLUDGE

For a feed with 10 wt-% solids, the effluent from the cooldown exchanger is at 330°C (626°F) and 3650 psi. It is hot enough to be used to generate a combination of 1200, 600, and 150 psi steam. For the preliminary process design, it was assumed that the process fluid would be used to generate all three levels of steam in three sequential heat exchangers (only one of which is shown in Figure 14).

The effluent from the cooler is separated into gaseous and liquid phases; any solids, if present, will have been trapped by and carried along with the liquid phase. The liquid phase is fed to a solid-liquid separator, from which solids are depressurized and stored prior to ultimate disposal. The liquid phase is depressurized and gaseous carbon dioxide is removed overhead from the medium pressure gas/liquid separator. The gaseous carbon dioxide is liquefied, as described below.

The aqueous phase from the medium pressure phase separator is then depressurized to atmospheric pressure, where a very small quantity of gaseous carbon dioxide and water vapor is released. This vent gas is clean. It could be discharged directly to the atmosphere (or, for an added measure of assurance, it could be passed through a bed of activated carbon).

The aqueous effluent from the atmospheric gas/liquid separator is clean water (typically less than 30 ppm TOC) with dissolved sodium chloride and calcium sulfate (typically less than 0.2 wt-% total dissolved solids). This aqueous effluent could be desalinated (by, e.g., reverse osmosis) to recover a highly purified water for reuse.

The gaseous phase from the first stage gas/liquid-solid separator is a mixture of excess oxygen and product carbon dioxide. The carbon dioxide is liquefied and separated from the excess oxygen (by a proprietary method); the excess oxygen is compressed to operating pressure, mixed with feed oxygen, and recycled.

The liquid carbon dioxide is sent to the by-product storage tank. The gaseous carbon dioxide from the medium pressure gas/liquid separator is liquefied and also sent to the by-product CO_2 storage tank. In practice, there could be two by-product storage tanks, each capable of holding 1 to 2 days production of carbon dioxide. When one tank is full, flow would be diverted to the other tank. The first tank would be sampled and analyzed for any residual contaminant. After passing analysis, it would be discharged. In the event that the by-product did not pass analysis, it could be recycled through the SCWO system for a second pass, or it could be passed through an activated carbon column. The carbon could then be oxidized in the SCWO system. By this procedure, any accidental release of

FIGURE 15. PULP MILL SLUDGE CHARACTERISTICS

Primary sludge (feed to primary tank)	75 BDT*/day 20% ash 3.3% wt-% BD solids
Secondary sludge (feed to blend tank)	25 BDT/day 18% ash 2.7% wt-% BD solids
Mixed feed from blend tank (primary and secondary)	3% wt-% BD solids
Output from screw presses (after dewatering)	40% wt-% BD solids
Heating value (dry basis)	7,000 Btu/lb

* bone dry ton

contaminants to the surrounding environment can be avoided. This unique feature of MODEC's SCWO process is expected to be a major benefit in situations where permitting is problematic.

B. Mass and Energy Balances and Equipment Sizing

A computer model for the flowsheet of Figure 14 has been developed by MODEC for calculating the mass throughputs and energy requirements of each equipment item. The model uses the ASPEN PLUS process simulator of Aspen Technology, Inc. MODEC has developed proprietary thermodynamic and transport models, which are used within ASPEN to provide estimates of density, enthalpy, phase equilibria, heat transfer coefficients and pressure drop. These proprietary models provide a significantly higher degree of agreement with experimental data than conventional models, especially in regions of high density fluids.

The characteristics of a typical pulp mill sludge are shown in Figure 15. The mass balance and the economics of the SCWO process are sensitive to the oxygen required to combust the sludge. MODEC did not have sufficient data to estimate the stoichiometric oxygen requirement, nor does ASPEN provide properties of sludge in the databank. Instead, a mixture of common materials was devised to approximate the stoichiometry and heating value of pulp mill sludge.

The method is illustrated in Figure 16. A mixture of pine bark and sewage sludge is used to simulate primary and secondary sludge, respectively. Note that a 75:25 mixture of (pine bark):(sewage sludge) provides excellent agreement on heating value (see step 3, Figure 16: 6,888 Btu/lb calculated vs. 7,000 Btu/lb of typical pulp mill sludge). The C:H:O ratios calculated for the bark-sewage mixture are then converted to an ash-free basis (step 4, Figure 16), from which a theoretical oxygen requirement of 1.15 ton O_2 per ton of sludge solids is calculated.

Highlights of the design are as follows:

Reactor Modules. The preheater, reactor, and cooldown exchangers are MODEC's proprietary design that prevents plugging of solids. The components were sized using MODEC's thermodynamic, heat transfer and kinetic models. The calculations were performed on the ASPEN PLUS computer system, wherein MODEC models were incorporated as user-written subroutines.

The 100 TPD system assumes that five 20 TPD reactor modules will be operated in parallel. MODEC believes that standardizing on 20 TPD modules will provide significant reductions in manufacturing and engineering costs. It will allow us to provide systems for 20 to 100 TPD capacities without requiring additional development cost (and time) beyond that required to build the first 20 TPD system.

Oxygen. At a 100 TPD dry sludge throughput, the oxygen requirement is 120 TPD. This level is about 4% above the theoretical; the primary loss of oxygen is as an impurity in by-product CO_2. This flowrate of oxygen was sized to provide a 20% excess of oxygen, above stoichiometric, in the reactor.

At a level of 120 TPD, it is more economical to purchase one's own air separation plant (or sign a long-term contract for supply from an over-the-fence system) rather than purchase liquid oxygen and have it delivered by truck. However, MODEC does not have reliable costs for a air separation plant or contract at this time. Therefore, MODEC has elected to use the following approach: (i) it was assumed that liquid oxygen would be purchased at $50/ton and (ii) the cost of storage and delivery was scaled, using a 0.6 factor, from a quote obtained for a system delivering 20 TPD of oxygen. It is believed that this approach provides a conservative (high) estimate for the cost of oxygen.

FIGURE 16. PULP MILL SLUDGE MODEL DEVELOPMENT

Basis: primary = 75 wt-%
secondary = 25 wt-%
total = 100 wt-%

ESTIMATION OF THE OXYGEN-TO-FEED RATIO FOR MIXED SLUDGE

1. Elemental compositions of sewage sludge and pine bark are used for CHO ratios of secondary and primary sludge, respectively.

	C	H	O	N	S	Ash	Btu/lb
Sewage sludge	14.2	2.1	10.5	1.1	0.7	71.4	2,040
Pine bark	52.3	5.8	38.8	0.2	0.0	2.9	8,780

2. The ash content is modified to reflect the values for pulp mill sludge.

	C	H	O	N	S	Ash	Btu/lb
Secondary sludge	40.7	6.0	30.1	3.2	2.0	18	5,849
Primary sludge	43.1	4.8	32.0	0.2	0.0	20	7,234

3. The ratio of 75:25 primary-to-secondary sludge is used to calculate the heating value of the modeled sludge mixture; the result is compared to the value of 7,000 Btu/lb, typical of pulp mill sludge.

	C	H	O	N	S	Ash	Btu/lb
Ave: 75% prim., 25% sec.	42.5	5.1	31.5	0.9	0.5	19.5	6,888

4. The ash-free composition is used to define the CHO ratios and the stoichiometric oxygen requirement.

	C	H	O	N	S	Ash	Btu/lb
Ash-free composition	52.8	6.3	39.1	1.1	0.6	0.0	8,556

Stoichiometric oxygen: 1.43 lb O_2/lb CHO = 1.15 lb O_2/lb solids

Steam Recovery. The effluent from the cooldown exchanger was used to generate 1200, 600, and 150 psi steam in three sequential, countercurrent steam generators. For 100 TPD of dry sludge, the steam recovery, as calculated from MODEC's ASPEN model[2] is estimated to be 7, 9, and 12 million Btu/hr for 1200, 600 and 150 psi steam,

[2]The present version of MODEC's ASPEN model does not include heat losses to the ambient. The steam recoveries here are discounted by 10% to adjust for the losses.

respectively. The recovered energy represent more than 45% of the heating value of the 10 wt-% sludge feed.

Carbon Dioxide Recovery. The 100 TPD sludge system would produce 140 TPD of CO_2 at about 95% purity. The refrigeration required to liquefy this CO_2 is provided by the evaporation of liquid oxygen. If desired, a high purity CO_2 liquid by-product could probably be produced.

To summarize, the major features of MODEC's SCWO process for treatment of pulp mill sludges are as follows:

- oxidation at 550 to 650°C provides greater than 99% combustion efficiency along with effective destruction of TOX and dioxins;
- minimal dewatering is necessary; sludge can be fed at 10 wt-% solids;
- regenerative heat exchange eliminates the need for auxiliary fuels;
- more than 45% of the sludge heating value is recovered as steam;
- recovery of carbon dioxide provides a substantial by-product credit;
- liquefaction of carbon dioxide eliminates the possibility of uncontrolled emissions and paves the way to rapid acceptability.

C. Preliminary Economic Analysis

Capital and operating cost estimates were prepared for pulp mill sludge treatment by SCWO. Capital costs were developed for 5, 20 and 100 ton/day of dry sludge solids using the following procedure:

(i) Major pieces of equipment were sized using the ASPEN PLUS model discussed in the previous subsection. Order-of-magnitude cost of each major equipment item was estimated using MODEC cost correlations.

(ii) Vendor quotes were obtained for those major equipment items that represent 10% or more of the total equipment cost.

(iii) Total installed costs were estimated by multiplying the cost of major equipment items by 4.

TABLE 11. CAPITAL COST ESTIMATES FOR 20 TO 100 TPD SCWO SYSTEMS

Equipment Item	20 TPD Cost	40 TPD Cost	60 TPD Cost	80 TPD Cost	100 TPD Cost
Pumps					
Reactors					
Tanks					
Heat Exchangers					
Liquid Oxygen System					
Phase Separators					
Instrumentation					
Process Control					
	1,510,000	2,450,000	3,320,000	4,170,000	5,040,000
Total Installed Cost	6,040,000	9,800,000	13,280,000	16,680,000	20,160,000

(iv) Installed costs were interpolated for sizes between 20 and 100 TPD and between 5 and 20 TPD by using appropriate exponents for cost as a function of size in the following formula:

$$Cost_2 = Cost_1 (Size_2/Size_1)^{Exponent}$$

Table 11 summarizes capital cost estimates for 20 to 100 TPD systems, using 20 TPD reactor-exchanger modules; Table 12 corresponds to 5 to 20 TPD systems, using 5 TPD reactor-exchanger modules. Note the difference in capital cost for a 20 TPD system built with four 5-TPD modules ($8 million) versus one 20-TPD module ($6 million). Although the total installed cost is higher, the multiple module approach is favored because it eliminates the technical risks of further scale up, resulting in the achievement of higher throughputs earlier into the commercialization phase.

The operating costs for treatment of pulp sludge by SCWO were based on the mass and energy balance results from MODEC's ASPEN simulations. Table 13 gives the estimated costs for a 100 TPD system. The expenditure before credits is $3,800,000, of which over 55% is for liquid oxygen. Resource recovery, in the form of steam, covers about 25% of the costs. Recovery and sale of by-product carbon dioxide can compensate for an additional 30% of the costs.

TABLE 12. CAPITAL COST ESTIMATES FOR 5 TO 20 TPD SCWO SYSTEMS

Equipment Item	5 TPD Cost	10 TPD Cost	15 TPD Cost	20 TPD Cost
Pumps				
Reactors				
Tanks				
Heat exchangers				
Liquid Oxygen System				
Phase Separators				
Instrumentation				
Process Control				
	$780,000	1,210,000	1,610,000	2,000,000
Total Installed Cost	$3,100,000	4,840,000	6,440,000	8,000,000

TABLE 13. SCWO OPERATING COSTS FOR A 100 TPD SYSTEM

Expenses		
Oxygen (120 TPD @ $50/ton)		$2,190,000
Electricity ($ 0.03/kw-hr x 7.35 x 10^6 kw-hr)		220,000
Labor (3/shift x 4 = 12 @ $44,000/person-year)		528,000
Residual solids landfilling (7,300 ton/yr @ $30/ton)		219,000
Maintenance (10% of capital equipment)		504,000
Cooling water (3,000 gpm = 1.6 x 10^9 gal/yr @ $.10/$10^3$ gal)		158,000
		$3,819,000
Credits		
CO_2 credit (130 ton/day @ 1.25 cents/lb)		(1,186,000)
Steam credit		
(7 MBtu/hr @ 1200 psi @ $5/MBtu)	$307,000	
(9 MBtu/hr @ 600 psi @ $4/MBtu)	315,000	
(12 MBtu/hr @ 150 psi @ $3/MBtu)	315,000	
		(937,000)
		($2,123,000)
Net O&M Cost		$1,696,000
Unit Cost ($/BDT)	=	48

TABLE 14. ANNUAL COST ESTIMATES FOR 20 TO 100 TPD SCWO SYSTEMS					
THROUGHPUT (TPD)					
MULTIPLES OF 20 TPD MODULES	20	40	60	80	100
Installed Cost	$6,000,000	$10,000,000	$13,600,000	$16,900,000	$20,200,000
ANNUALIZED COSTS					
Cost of Capital (12%, 10 yr)	1,067,000	1,731,000	2,354,000	2,958,000	3,575,000
Maintenance (10% of equip. cost)	153,000	250,000	339,000	423,000	504,000
Operating Direct Labor	352,000	396,000	440,000	484,000	528,000
Supplies					
Oxygen	613,000	1,139,000	1,577,000	1,927,000	2,190,000
Electricity	38,000	76,000	115,000	153,000	220,000
Cooling Water	32,000	63,000	95,000	126,000	158,000
Residual Solids Disposal	44,000	88,000	131,000	175,000	219,000
Annual Cost	2,299,000	3,743,000	5,051,000	6,244,000	7,394,000
ANNUALIZED CREDITS					
Steam Production	(187,000)	(375,000)	(562,000)	(750,000)	(937,000)
Carbon Dioxide by-Product	(237,000)	(474,000)	(712,000)	(949,000)	(1,186,000)
Annual Credit	(424,000)	(849,000)	(1,274,000)	(1,699,000)	(2,123,000)
Annual Net Cost	1,875,000	2,894,000	3,777,000	4,545,000	5,271,000
Unit Cost ($/dry ton)	26[illegible]	207	180	162	151

For a 100 TPD facility, the net O&M costs are estimated to be about $50/BDT, which is less than the cost of dewatering sludge to 40 wt-% solids. Table 14 shows the annual costs from 20 to 100 TPD and Table 15 shows the same for systems of 5 to 20 TPD.

D. COST COMPARISONS

Having developed preliminary cost estimates for SCWO treatment of pulp mill sludge, cost comparisons of landfilling, incineration, and SCWO can be made on comparable bases. In this section, the landfilling and incineration cost estimates presented in Section III are used to examine three cases, representing the following scenarios:

Case 1. A large mill in the northeast or midwest region of the U.S., producing 100 TPD of dry sludge solids, considers three alternatives:

(i) Dewatering with screw presses to 40 wt-% solids, followed by trucking of the sludge to a nearby landfill;

TABLE 15. ANNUAL COST ESTIMATES FOR 5 TO 20 TPD SCWO SYSTEMS

THROUGHPUT (TPD)	5	10	15	20
Installed Cost	$3,100,000	$4,830,000	$6,450,000	$7,990,000
ANNUALIZED COSTS				
Cost of Capital (12%, 10 yr)	549,000	854,000	1,142,000	1,414,000
Maintenance (10% of equip. cost)	78,000	121,000	161,000	200,000
Operating Direct Labor	352,000	352,000	352,000	352,000
Supplies				
Oxygen	186,150	350,400	492,750	613,200
Electricity	9,550	19,100	28,650	38,200
Cooling Water	7,900	15,800	23,700	31,600
Residual Solids Disposal	10,950	21,900	32,850	43,800
Annual Operating Cost	1,193,550	1,734,200	2,232,950	2,692,800
ANNUALIZED CREDITS				
Steam Production	(46,850)	(93,700)	(140,550)	(187,400)
Carbon Dioxide By-product	(59,300)	(118,600)	(177,900)	(237,200)
Annual Credit	(106,150)	(212,300)	(318,450)	(424,600)
Annual Net Cost	1,087,400	1,521,900	1,914,500	2,268,200
Unit Cost ($/dry ton)	621	435	365	324

(ii) Dewatering with screw presses to 40 wt-% solids, followed by on-site incineration at 2200°F; or

(iii) Dewatering with a centrifuge to 10 wt-% solids, followed by on-site SCWO treatment.

Case 2. A large mill in the northwest or southeast region of the U.S., producing 100 TPD of dry sludge solids, considers the same three options as in Case 1.

Case 3. A small mill in the northeast or midwest, producing 10 TPD of dry sludge solids, considers two alternatives:

(i) Dewatering to 20 wt-% solids using a rotary vacuum filter, followed by disposal off-site via a contractor; or

(ii) Dewatering with a centrifuge to 10 wt-% solids,, followed by on-site SCWO treatment.

TABLE 16. 100 TPD COST COMPARISONS (Cases 1 and 2)

Assumptions	Tipping Fee ($/yd^3)	Fuel Cost ($/MBtu)	Power Cost ($/KwH)
Case 1	35	5	0.05
Case 2	10	3	0.03

Option	Dewater to 40% Solids + Landfill	Dewater to 40% Solids + Incinerate	Dewater to 10% Solids + SCWO
Case 1			
Capital Cost	$4,000,000	$21,000,000	$20,200,000
Annual O&M Cost	7,070,000	8,015,000	2,017,000
Unit Cost ($/BDT)	213	330	160
Case 2			
Capital Cost	$4,000,000	$21,000,000	$20,200,000
Annual O&M Cost	3,395,000	6,310,000	1,696,000
Unit Cost ($/BDT)	108	275	151

The parameters used for tipping fees, fuel and electricity costs for each of the scenarios are shown in Tables 16 and 17, along with estimates of the unit cost ($/BDT) assuming a 12% cost of capital and a 10-year useful life of any hardware purchase. [The assumption of 10-year life reflects the view that changes in waste treatment regulations can force technology changes long before the useful life of hardware is reached.]

The major differences between regions of the U.S. is assumed to continue to be the differences in the cost of landfilling, as reflected in tipping fees. In the northeast and midwest, a range of $35 to $75/yd^3 is assumed, with larger mills paying the lower fee and smaller mills paying the higher one. For the northwest and southeast, a tipping fee of $10/yd^3 is assumed.

It is MODEC's belief that these assumed costs for landfilling are very conservative if one is considering options for 1995 to 2000. Indeed, there is real concern by some in the industry that landfilling may not be an option at any cost in the not-too-distant future.

TABLE 17. 10 TPD COST COMPARISONS (Case 3)			
Assumptions	Tipping Fee ($/yd^3)	Fuel Cost ($/MBtu)	Power Cost ($/KwH)
Case 3	75	5	0.05

Option	Dewater to 20% Solids + Landfill	Dewater to 10% Solids + SCWO
Case 3		
Capital Cost	$250,000	$5,000,000
Annual O&M Cost	3,444,000	685,400
Unit Cost ($/BDT)	984	440

The costs for Case 1 (Table 16) show that SCWO is clearly more cost-effective than incineration. Given that the first costs of the two are comparable, the only advantage incineration has is that it is already available commercially.

With respect to landfilling, an investment analysis is required to determine the rate of return on the additional cost of the SCWO system versus the savings in O&M cost. Such an analysis is shown in Table 18. The scenario is that the large mill in the northeast or midwest (Case 1) faces a decision for 1995 (the first year that a 100-TPD SCWO unit will probably be available commercially). Even with a conservative life of 10 years, the SCWO option can return 25% on the investment of added capital above the landfilling option. Thus, MODEC anticipates that large pulp and paper companies with extensive operations in the northeast and midwest are potential clients for first-generation 100 TPD systems.

The costs for Case 2 (Table 16) show that landfills will continue to be the most economical alternative as long as tipping fees in the range of $10/yd^3 are available. For large mills in the northwest and southeast, the only incentive to seek oxidation alternatives is the need to keep one's options open in the face of unpredictable regulations governing land disposal. When oxidation options are sought, it is clear that SCWO is far more cost-effective than incineration.

The costs for Case 3, shown in Table 17, once again require a return-on-investment analysis for comparing the SCWO option to landfilling for the small mill in the Northeast or Midwest. Table 19 shows the results of that analysis for a mill looking ahead to a 1995 startup. Clearly, the SCWO unit provides a substantially better choice than landfilling solely on the basis of economics. Thus, MODEC believes

TABLE 18. RETURN ON INVESTMENT FOR A LARGE MILL PURCHASING A 100 TPD SCWO SYSTEM

Case 1 Basis: 1995 costs assume 5%/yr inflation in capital cost
Dewater on site
Pay \$35/yd^3 tipping fee for transportation and landfilling

Year	(a) Dewater to 40% solids + landfill @ \$35/yd^3 (\$)	(b) Dewater to 10% solids + SCWO with five 20 TPD units (\$)	Savings (a) - (b) (\$)
1995	5,105,000	25,780,000	(20,680,000)
1996	7,455,000	1,750,000	5,705,000
1997	7,455,000	1,750,000	5,705,000
1998	7,455,000	1,750,000	5,705,000
1999	7,455,000	1,750,000	5,705,000
2000	7,455,000	1,750,000	5,705,000
2001	7,455,000	1,750,000	5,705,000
2002	7,455,000	1,750,000	5,705,000
2003	7,455,000	1,750,000	5,705,000
2004	7,455,000	1,750,000	5,705,000
2005	7,455,000	1,750,000	5,705,000
Internal rate of return = 25%			

that its SCWO units with capacities as low as 10 TPD can have a significant market as soon as commercial viability can be demonstrated.

Having shown that SCWO is not only an environmentally-acceptable alternative, but also a cost-effective one, MODEC's near term objective is to scale up to commercially viable sizes as expeditiously as possible. Feedback from the industry indicates that there remain two key questions:

(1) Can SCWO systems operate safely and reliably over long duration with minimal operator attention? and

(2) Are the results obtained to date scalable to commercial throughputs?

TABLE 19. RETURN ON INVESTMENT FOR A SMALL MILL PURCHASING A 10 TPD SCWO SYSTEM

Case 3 Basis: 1994 costs assume 5%/yr inflation in capital cost
Dewater on site
Pay $75/yd^3 tipping fee for off site disposal

Year	(a) Dewater to 20% solids + landfill @ $75/yd^3 ($)	(b) Dewater to 10% solids + SCWO with two 5 TPD units ($)	Savings (a) - (b) ($)
1994	122,000	5,830,000	(5,710,000)
1995	3,444,000	668,500	2,775,500
1996	3,444,000	668,500	2,775,500
1997	3,444,000	668,500	2,775,500
1998	3,444,000	668,500	2,775,500
1999	3,444,000	668,500	2,775,500
2000	3,444,000	668,500	2,775,500
2001	3,444,000	668,500	2,775,500
2002	3,444,000	668,500	2,775,500
2003	3,444,000	668,500	2,775,500
2004	3,444,000	668,500	2,775,500

Internal rate of return = 48%

MODEC believes that both of these questions can be answered affirmatively. Following automation of the bench scale prototype, a program is planned to demonstrate operation over prolonged periods in a pulp mill environment. In parallel, MODEC plans to conduct a detailed design and engineering package for a 5 TPD pilot plant, to be built, debugged and demonstrated within the next 2 years. This timetable should position MODEC to offer smaller commercial units (e.g., 10 to 20 TPD) for delivery in 1993 and larger units in the 1994 time frame.

VII. CONCLUSIONS

A. SLUDGE GENERATION AND DISPOSAL

Large quantities of aqueous waste are generated in the U.S. and throughout the world. Sludges are the ubiqitous by-product of aqueous waste treatment. The more stringent the treatment requirements, the more sludge that is generated.

Landfilling and ocean dumping, the two traditional methods of sludge disposal, will not be viable options much longer. Incineration is the only alternative now commercially available for destroying the organic components of sludges. For sludges that are difficult to dewater, incineration consumes large quantities of auxiliary fuel and is expensive.

B. MODEC'S PROCESS FOR SLUDGE DESTRUCTION

Supercritical water oxidation is more energy-efficient, cost-effective and environmentally-acceptable than incineration for industrial and municipal sludges. SCWO is now cost-competitive with landfilling of sludges in the northeast and midwest regions of the U.S. MODEC's SCWO process can treat pulp mill sludges and effectively destroy chlorinated organics, including dioxins. MODEC has solved the technical problems that have heretofore prevented commercialization of SCWO technology. MODEC has developed non-plugging, continuous-flow reactors and means for separating inorganic solids from a clean aqueous effluent.

Subsequent phases of this DOE project will involve demonstration of MODEC's SCWO process for pulp mill sludge treatment. One objective is to operate MODEC's bench prototype around-the-clock for prolonged periods so as to demonstrate safe and reliable operation. A second is to build a pilot unit to demonstrate that the process can be scaled to commercially significant throughputs. Beyond that, MODEC plans to make its process commercially available by 1993.

VIII. REFERENCES

Blosser, R.O. and Miner, R.A., Sludge Handling and Disposal Practices in the U.S. Pulp and Paper Industry, Presented at Environmental Protection in the 90's EUCEPA Symposium, Helsinki, May 19-22, 1986.

Modell, M., Gasification and Liquefaction of Forest Products in Supercritical Water, Chapter 6 in Fundamentals of Thermochemical Biomass Conversion, Elsevier Applied Science, 1985(1).

Modell, M., Processing Methods for the Oxidation of Organics in Supercritical Water, U.S. Patent No. 4,543,190, September 24, 1985(2).

Modell, M., Supercritical Water Oxidation, Chapter 8-11 in Standard Handbook of Hazardous Waste Treatment and Disposal, Harry M. Freeman, ed., McGraw Hill, 1989.

Thomason, T.B. and Modell, M., Supercritical Water Destruction of Aqueous Wastes, Hazardous Waste, Vol. 1, No. 4, 1984. pp. 453-467.

Timberlake, S.H., Hong, G.T., Simson, M. and Modell, M., Supercritical Water Oxidation for Wastewater Treatment: Preliminary Study of Urea Destruction, SAE Paper 820872.

U.S. Congress, Office of Technology Assessment, Technologies for Reducing Dioxin in the Manufacture of Bleached Wood Pulp, OTA-BP-O-54 (Washington, DC: 1989).

U.S. Environmental Protection Agency, Development Document for Effluent Limitations Guidelines and Standards for the Pulp, Paper, and Paperboard and the Builders' Paper and Board Mill: Point Source Categories, EPA 440/1-82/025 (Washington, DC: 1982).

U.S. Environmental Protection Agency, National Dioxin Study, EPA/530-SW-87-025 (Washington, DC: 1987).

U.S. Environmental Protection Agency, U.S. EPA/Paper Industry Cooperative Dioxin Screening Study, EPA 440/1-88-025 (Washington, DC: 1988).

IX. GLOSSARY OF ACRONYMS

AOX	Adsorbable organic halide
BDT	Bone dry ton
BOD	Biological oxygen demand
cc/min	Cubic centimeters per minute
DE	Destruction efficiency
DRE	Destruction/reduction efficiency
EOX	Extractable organic halide
gpd	Gallons per day
IX	Inorganic Halide
MEK	Methyl ethyl ketone
NCASI	National Council on Air and Stream Improvement for the Pulp and Paper Industry
ND (x)	Non detectable; Value measured was below detectable limit, x
O&M	Operating and maintenance
PCB	Polychlorincated biphenyls
POTW	Publicly owned treatment works
ppb	Parts per billion
ppt	Parts per trillion
SCFM	Standard cubic feet per minute
SCW	Supercritical water
SCWO	Supercritical water oxidation
TCDD	Tetrachlorodibenzodioxin, commonly called dioxin
TCDF	Tetrachlorodibenzofuran
TCLP	Toxicity characteristic leaching procedure
TOC	Total organic carbon
TOX	Total organic halide
TPD	Tons per day
TSS	Total suspended solids
TX	Total Halide
WAO	Wet air oxidation

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