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TOXIC COMBUSTION BY-PRODUCTS: GENERATION, SEPARATION, CLEANSING, CONTAINMENT

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TOXIC COMBUSTION BY-PRODUCTS: GENERATION, SEPARATION, CLEANSING, CONTAINMENT

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ABSTRACT

The focus of this paper is on the diagnosis, control, and containment of potentially toxic combustion by-products when mixed wastes are treated at elevated temperatures. The classes of potentially toxic combustion by-products discussed fall into several categories—acid gases, particulate matter, inorganic metals, and organics. Radionuclides are treated as a subset of inorganic metals, while organics are divided into two subclassifications—products of incomplete combustion (PICs); and principal organic hazardous constituents (POHCs).

An extended flue gas cleaning system is described which can be used to contain potentially toxic organic emissions and recycle the hazardous materials for further treatment. The proposed system utilizes oxygen, rather than air, to reduce the total quantities of emissions, improve the efficiency of oxidation reactions, and minimize the emissions of NOx. Flue gas recycling is used to obtain the cooling normally performed by nitrogen in the combustion air and to provide a simple mechanism for containing all potentially toxic emissions. Three thermal treatment unit operations are used in series to obtain more effective process control. Similarly, three emission separation and containment unit operations are used in series in the toxic emission containment system. Most of these technologies have been used extensively in industry for similar feed rates and composition. While the proposed application is unique, the operating environment is no more severe than most industrial applications employing the subject technology. For this reason, reliability, availability, maintainability, and safety considerations should not present new areas of uncertainty.

Real time diagnostic hardware and software are used to ensure that all products released are not harmful to the environment. Should excess levels of toxic emissions be generated during thermal treatment, provisions have been made for automatic storage, separation of hazardous materials, commodity regeneration, and recycling of potentially harmful constituents. Additionally, the greenhouse gas, carbon dioxide, normally associated with high temperature processing, is recovered and not directly emitted to the atmosphere.

EXISTING FLUE GAS MONITORING PROBLEM

Emphasis on the inability to continuously monitor toxic combustion by-products has detracted from the efforts associated with defining maximum achievable control technology. One recent perception of hazardous waste incineration is in technical literature which is replete with evidence of uncontained toxic by-products of combustion; there is an absence of reliable continuous emission monitors for priority toxic compounds; and quantitative risk assessments are "mathematics masquerading as science" [1]. Essentially the same issues were raised, and similar conclusions drawn, in a U.S. Environmental Protection Agency (EPA) report issued October 1989 [2]. This report recognized that the continuous monitoring devices used to analyze total hydrocarbons in flue gases understate by 25% the hydrocarbons present when compared with noncontinuous, more comprehensive analysis. The report further expressed the concern that there is a probability that the deficiency may occur in the semivolatile and nonvolatiles categories. These categories represent only 1% of total hydrocarbons (THCs) in the EPA database but pose 80% of the cancer risk. This overall problem is exacerbated due to the hammer provisions mandated in the Clean Air Act Amendments (CAAA) of 1990 which require EPA to promulgate Most Achievable Control Technology (MACT) industry standards for hazardous air pollutants beginning in 1997. The method currently being advanced by EPA to define MACT is to identify the best 12% (or best 5 emission sources, whichever is greater) within each industrial sector and then determine the technology utilized to achieve the low emissions [3].

Another more universal approach to defining MACT is to utilize technology capable of removing the inert ingredients of flue gases (water, nitrogen, and carbon dioxide) from the numerous quixotic potentially toxic emissions and recycling the relatively small amount of potentially toxic substances so they can be destroyed by further treatment or permanently contained. Currently, it is estimated that the best demonstrated available technology (BDAT) hazardous waste incinerators normally emit 250 parts per million (ppm) of potentially toxic emissions (PTEs) to the atmosphere. About 10%, 25 ppm, of these emissions are organic compounds perceived to be the major source of carcinogens. Of the hundreds of products of incomplete combustion (PICs) found in a given stack test, less than 10 compounds were common to multiple site tests. It can be demonstrated that it is not necessary to measure precisely these organic substances, especially the potentially more lethal dioxin-like compounds, to contain these substances within the thermal treatment configuration.

BACKGROUND

This paper presents an approach to overcoming this effluent measurement dilemma and features enriched oxygen combustion, flue gas recycle, and product extraction. To contain the PTEs, it is necessary to understand their generation as well as their pathways through the process. One must start with the data extracted from the reports issued by EPA which address the quantities and composition of the PTEs emitted from hazardous waste incinerators. In sum, these reports subdivide PTEs into the following classifications: acid gases, particulate matter, metals, and organics. For the purposes of this paper, radionuclides are classified as metals.

The majority of the EPA reports focused on particulate matter, metals and organics. The preponderance of information gathered dealt with organic matter: PICs and POHCs. Much of these data were collected in the 1980s when EPA was mandated to establish national emission standards for hazardous air pollutants (NESHAP). The CAAA of 1990 abandoned this regulatory scheme for an approach based upon technology alternatives. Since then, air emission data has been limited to particulate matter (PM) and dioxin/furan emission levels.

For the stated objectives, the 1980s data bank needs to be condensed and the post-1990 data bank needs to be enhanced. Also, the evolution of sampling and analysis methodology requires that a few basic definitions be established. This is accomplished in the next section.

GENERATION OF POTENTIALLY TOXIC EMISSIONS

Figure 1 shows the acid gas, particulate matter, metals and organic pathways before, during, and after combustion. Evaporation, vaporization, and thermal cracking of organic constituents all occur prior to combustion regardless of the manner in which the feedstock is introduced into the combustion chamber. Most hazardous waste feedstocks contain metals, organics, water, and inert minerals; therefore, it is reasonable to assume that the typical airborne droplet contains all these constituents. During combustion, only the organics are destroyed; the water and inert minerals remain compositionally intact. Inorganic elements, for the most part, recombine with other inorganic specie, primarily acids and salts (metal compounds). Acids are threshold pollutants and rarely, if ever, leave an incinerator above the specified limit, regardless of the quantities fed and the manner in which the incinerator is operated because, whatever the quantity generated during the combustion reactions, these quantities are readily neutralized and reduced to a value below the threshold limit in the air pollution control system (APCS). The situation with the salts is less straightforward. Some salts fall within the threshold risk assessment classification; others do not. The latter nonthreshold category is frequently referred to as carcinogens or, within the NESHAP classification scheme, as "metals", a term used to refer to the quantity of metal specie present in all salt forms.

With the exception of organic destruction, specific chemical reactions cannot be controlled. Due to the abundance of oxygen present, about 60% of all metals are converted to oxides and leave with the bottom ash; the remaining metals combine with available anions to form airborne salt complexes. These remaining salt complexes have more complex removal mechanisms in an APCS than the acid classification, thus giving greater concern for overall metal removal efficiencies. While metal air emission quantities remain below the NESHAP standards, concern remains due to the impracticality of measuring total metal input and the bottom and fly ash output. Studies conducted in the late 1980s provide insight into the partitioning of these constituents throughout the incineration configuration.

Central to this discussion is the definition of particulate matter. Figure 1 shows the generation mechanisms for toxic substances. Homogenous and heterogenous acid, salt, and organic flume nuclei are included within the definition of particulate matter because this is the normal current sampling and analysis practice. During the 1970s, the normal sampling and analysis practice was to include only the fly ash constituents. To ensure containment, it is necessary to estimate the quantities and composition of each particulate matter component. Further, since the fly ash component can be 1000 times larger than the quantity of condensed acid, metal, and organic fume nuclei, it should be removed first; otherwise, metal and organic separation efficiencies will decrease.

Figure 1 depicts fly ash being conveyed from the solid bed of material into the gas stream. This action should be minimized, to the extent possible, by reducing gas velocities and aggressive in-bed combustion techniques. Excessive fly ash interferes with the combustion reactions and increases the probability of increased toxic organic emissions. A common perception is that a combustion chamber is at a uniform temperature—it is not. The temperature differential may be 800°F, with the solid feedstock being the coldest material in the chamber. Premature solid removal via gas conveyance interferes with the desired heat transfer and chemical reaction mechanisms.

Currently, 10 ppm to 2000 ppm of organic substances, and between 365 ppm to 45,000 ppm of metal substances, are found in hazardous waste incinerators bottom ash [4]. The presence of metals is unavoidable if they are present in the waste feedstock. The presence of organic substances indicates an inadequate solid feedstock residence time. In the proposed configuration, the organic materials will be destroyed and the metals will be stabilized when the bottom ash drops directly into a vitrifier. Focus should remain on the flue gases containing the NESHAP pollutants and exiting the APCS after passing through the secondary combustion chamber.

Using the mass balance produced at the feed rate used for this presentation, which is defined later, the previously mentioned PM emission rate of 0.012 gr/dscf can be converted to an absolute value of 1.35 lbs/hr

(26 ppm). A conservative approach will be used in that the PM quantities will be only for fly ash (inerts). Fume nuclei (acid, metals, organics) will be evaluated separately.

The general category of potentially toxic combustion by-products has previously been estimated to represent up to 250 ppm of the total combustion by-products being emitted to the atmosphere. For ease of quantification and understanding, this general category has been divided into four subcategories: acid gases, particulate matter, metals and organics. Each category will be addressed separately in subsequent sections.

Acid Gases

It is not practical to precisely quantify the amount of acid gas feedstocks entering an incinerator in most instances. Nevertheless, the pathways and removal efficiencies for these low level toxic threshold combustion by-products are efficient and well understood. Acid gases rarely, if ever, escape at concentrations above the national standard threshold limit, even though they can represent up to 80% of the potentially toxic combustion by-products emissions. Regardless, before product separation can be achieved, these acid gas residuals must be removed in the extended flue gas cleaning system.

Particulate Matter

As noted in the section addressing the generation of PTEs, the manner in which PM is collected and analyzed has evolved over the last 25 years. Currently and most frequently, PM data includes both the metal and organic category quantities. In this assessment, the term PM will be used to denote only the inert mineral (fly ash) components. This assumption, will on occasion, overstate the quantities of fly ash present in the combustion by-products. The potential overstatement will not affect the conclusions reached in this analysis.

Figure 2 shows a profile of the PM generated throughout the Hazardous Waste Industry (HWI). The median PM emissions for the industry is 0.012 grain per dry standard cubic feet (gr/dscf) adjusted to a 7% 0_2 level. Figure 2 also shows considerable test variability. The maximum value for the median population was 0.02 gr/dscf, adjusted to 7% 0_2 which also represents the minimum value when 90% of the HWI industry is taken into consideration. Since the stated objective is to focus on typical rather than extreme points, the value of 0.02 gr/dscf is used in this assessment as a representative value for inert mineral (fly ash) emissions.

Figure 2 depicts a relatively wide variability (nearly threefold) in multitest results at the same site. While nonsteady state operations can produce this phenonemon, a more likely situation is that this variability is due to feedstock variations. At these low PM concentration levels, a threefold variation will not have significant operational or containment impact.

Metals

During the 1970s, little was known about the various metal pathways through a hazardous waste incinerator. During the late 1980s, EPA and several major corporations sponsored programs to identify these pathways [5; 6; 7; 8; 9; 10]. An overview of these findings is presented in succeeding paragraphs. Table 1 lists the removal efficiencies for the metals of interest.

TABLE 1

Metal Removal Efficiencies

Metal Specie	Case 1[2]	Case 2[7]	Case 3[6]	Case 4[3]
Silver	98.91	99.99		96
Arsenic	99.98	95.57	82	95
Barium	99.90	99.68		96
Beryllium	98.80		92	96
Cadmium	99.71	87.65	82	95
Chromium	99.53	97.22	90	98
Mercury	75.88	96.37		50
Iron		99.80		
Potassium		94.83		
Sodium		90.99		
Lead	99.89	93.20	80	95
Antimony	98.75			95
Thallium				95
Zinc		95.34		

Four sets of removal efficiencies are presented to reflect the differences in equipment configurations. Case 1 represents an APCS configuration which contains a fabric filter followed by a venturi scrubber and a packed tower. Case 2 shows the results obtained from operating four types of wet scrubbers in series (catenary grid, wet electrostatic precipitator, packed tower, coalescing filter). Case 3 reflects the removal efficiencies obtained when only two types of wet scrubbers are used in series (venturi scrubber, packed tower). Case 4 depicts the values anticipated in the EPA guidance document.

The most interesting finding in these research endeavors was the quantity of metals which remained in the bottom ash in the form of oxides. In general, chlorine content does not significantly impact the metal emissions leaving the stack. However, chlorine content, operating temperature, and particulate matter does impact metal partitioning between the incinerator bottom ash and the air pollution control configuration residues. Case 3 shows that higher chlorine content shifts the metal residues from the combustor to the APCS between 0-15% depending on the metal specie in question. Due to the differences in process configurations and feed composition, partitioning information between the combustion chamber and the flue gas cleaning system contains significant variations. Stack emissions are more constant. Nominal partitioning percentages between the combustor, the APCS and stack are 60%, 30%, and 10% respectively.

In the proposed extended flue gas cleaning system, the split between the combustor and the APCS residues is of little consequence as both streams are ultimately transformed into a stable, environmentally secure composite after being treated in the vitrifier, which operates in tandem with the combustor. This process modification will increase the toxic metal emissions in the off-gas to approximately 15% of the total metals fed. Eventually, most of these toxic metal emissions will be collected in the extended flue gas cleaning system and removed as solids. After sampling and analysis, the solids can be disposed or recycled to the vitrifier.

While process configuration, operating conditions, and feed composition are parameters which affect the quantities of toxic metal emissions (TME) generated, but not necessarily released through the APCS, the critical control parameter is the amount of metals fed into the combustion chamber. Within the processing system, TME pathways are much more constrained than the toxic organic emission (TOE) pathways. Both the TME and TOE pathways and requisite containment criteria will be presented.

Organics

Normally, organic emissions never exceed 25 ppm of the total by-products of combustion. Nevertheless, the makeup of these 25 ppm remains most controversial. In part, the controversy emanates from the inability to 1) identify all of the hundreds of organic specie believed to be present in this 25 ppm; and 2) obtain a reliable on-line value for all of the intermediate organics, the most likely source of carcinogens, believed to be present. Much attention was given to these deficiencies in the late 1980s while EPA was attempting to establish the mandated NESHAP standards. Regardless of the technological and operational deficiencies encountered during the establishment of NESHAP standards, adequate information has been compiled over the last decade to differentiate reliable from inconsistent data. Succinctly stated, the more reliable data is associated with the volatile contaminants while the less reliable data is associated with the semivolatile and nonvolatile contaminants. The following table shows that boiling point temperatures are used to separate these contaminant categories.

TABLE 2
Volatility Classifications

Classification	Boiling Point (°C)
Volatile	30 (86°F)-100 (212°F)
Semivolatile	100-300 (572°F)
Nonvolatile	>300 (572°F)

These three volatility categories apply equally to all organic hazardous constituents: POHCs and PICs. It is not practical to distinguish between individual PIC and POHC specie while attempting to continuously monitor the critical organic toxic substances which may be in the flue gases at minute levels. More *importantly, the continuous measurement of all organic toxic substances is not required to ensure containment.* The critical attribute is the containment of all (toxic and nontoxic) semivolatile and nonvolatile organic substances because of the major known carcinogens found in these categories.

It is important to note that the aforementioned organic constituent classification scheme is administratively rather than naturally ordained. The reason for the administrative partitioning is that it coincides with the off-line sampling and analytic methods recommended by EPA. The EPA Level 1 monitoring system is comprised of total volatile organics (C_1-C_6); total semivolatile organics (total chromatographable organics [TCO]); and total nonvolatile organics (gravimetric [GRAV]) and is presumed to account for all hydrocarbons emissions. Frequently, a flame ionization detector (FID), the instrument most frequently used as an on-line monitor to detect organics present in the flue gases is referred to as a continuous total hydrocarbon monitor. More accurately, it is a reliable volatile hydrocarbon detector. FID results are based upon a weighted average response factor which, in turn, is based upon a standardized general list of compounds emitted from the incinerator. In actual practice, the composition of the organic compounds vary from the standardized list used to calibrate the instrument. Semivolatile and nonvolatile compounds may be included on occasion. When FID results are compared with EPA Level 1 results, the FID accounts for about 75% of the THC. While EPA Level 1 results represent an accurate assessment of THC present, some 10% to 20% of the individual specie could not be identified. Most of these unknown specie are in the semivolatile and nonvolatile categories.

Recently, EPA sponsored two in-depth PIC analysis projects [11; 12]. Both projects attempted analysis for some 100 PICs. One project was site specific; the other was a synthesized review of data collected previously on numerous hazardous waste combustion configurations. A significant finding was that some 50% of the quantity of PICs generated emanated from eight aliphatic volatile specie, mostly C_1s and C_2s. Benzene was the only aromatic volatile in this group. Naphthalene was the only semivolatile compound consistently present. The average fraction of unknown hydrocarbons was 25% and 35% for the respective industry-wide and site-specific incinerator studies. The industry-wide study results demonstrated the following volatility allocation: 1) volatiles, 81%; 2) semivolatiles, 15%; and 3) nonvolatiles, 4%. The site specific study only allocated the particular pollutant specie which were identified and measured (i.e., there were no unknown specie or nonvolatile specie allocated). The site specific PIC average allocation was 50% for the volatiles and semivolatiles.

One of the objectives of the site-specific study was to obtain more relevant PIC information during transient combustion periods. The concern was that an FID monitor was not adequate for detecting excessive PIC emissions, especially semivolatile and nonvolatile PICs. Three test runs were made for both steady-state and transient conditions. The significant results are reflected in Table 3.

TABLE 3
Toxic Organic Emissions
Steady State vs. Transient Conditions

Toxic Emission Categories	Steady State Averages		Transient Averages		Percent Increase	
Total hydrocarbons* (ppm) ***(FID Equivalent)**		6.9		87		1161
Methane[6]		1.4		49		3400
Select Volatiles						
Priority pollutants (21**) ****(Number of pollutants analyzed)**	260.4		281.4			
Nonpriority pollutants (23)	4.3		4.8			
Totals (44)		264.7		286.2		8.12
Select Semivolatiles (%)						
Oxygenated aliphatics (35)	65.21		73.86		13.26	
Chlorinated aliphatics (3)	16.50		9.11		-44.79	
Aliphatic hydrocarbons (3)	1.01		1.27		25.74	
Aromatic hydrocarbons (4)	3.02		8.58		184.11	
Unknown compounds (20)	14.26		7.18		-49.65	
Totals	100.0		100.0			
Totals (65) mg/m^3*** *****(mg/m^3 is about 10 fold ppb)**		2679		2284		-14.74

As expected, the values for methane and total hydrocarbons, as measured by separate FIDs, increased dramatically during transient combustion periods. Also expected was that the quantities of volatile pollutants present during transient combustion periods increased. Totally unexpected was the corresponding decrease in the quantity of semivolatiles present during transient conditions. Regardless, this variance is not a critical value for the present analysis.

The purpose of this detailed analysis is to couple priority pollutants with the volatility of all organic constituents which, in turn, can be directly related to two critical separation parameters: molecular weight and physical structure. Molecular weight is the more important parameter for achieving the stated objectives. The linchpin between molecular weight and volatility is the number of carbon atoms in a molecule. Table 4 shows the relationship between the number of carbon atoms, the molecular formula, and the number of different physical formulas possible for compounds containing only carbon and hydrogen. It should also be noted that there are many compounds of interest which contain more than 25 carbon atoms.

TABLE 4
Molecular vs. Structural Formulas

Number of Carbon Atoms	Molecular Formula	Number of Structural Formulas
1	CH_4	1
6	C_6H_{14}	355
12	$C_{12}H_{26}$	4,347
18	$C_{18}H_{38}$	60,523
25	$C_{25}H_{52}$	36,797,588

It should be clear that when other inorganic elements are substituted for hydrogen, the number of potential structural formulas increases exponentially.

In dealing with such a vast array of structures, organic chemists have traditionally analyzed these structures according to the number of carbon atoms present within a basic structure category after a base structure has been defined. After definition, the base structure is then graduated in terms of a CH_2 radical. The base structure plus all the incremental CH_2 components is called a homologous series. Table 5 shows a partial listing of the homologous series of paraffin hydrocarbon with the general equation of C_nH_{2n+2}. The concept of an homologous series is of importance because it has been found that the physical and chemical properties of homologues gradually change within a homologous series. In addition, it has been shown that all organic compounds may be classified into homologous series [13]. Table 5 shows boiling points for most of the homologues which contain the priority pollutants of concern.

The physical properties of the specie within any homologous series generally undergo a uniform change as the molecular weight increases. The addition of a $-CH_2$ group usually increases the boiling point 19°C. In a homologous category, the normal straight-chain structure invariably possesses the highest boiling point. Branching the chain decreases the boiling point; isocompounds in general decrease the boiling point about 9°C and, of two isometric compounds, the more highly branched chain structure is the more volatile.

HYDROCARBONS							OXYGENATED			SULFURS	NITROGEN		AROMATICS		
PARAFFINS				OLEFINS	ALKINES	CYCLO HYDRO-CARBONS	ALCOHOL	ETHERS	IODINE	MERCAPTANS	AMINE	AMIDES	BENZENE	NAPTHALENE	ANTHRACENE
IDENTIFYING FEATURE			$-CH_2$	C=C	C≡C	RING	C–OH	C-O-C	$C-I_n$	C-S-	C-N-	$C-NO_n$	(1 RINGS)	(2 RINGS)	(3 RINGS)
CLASSIFICATION	MOLECULAR FORMULA	MOLECULAR WEIGHT	BOILING POINTS												
Methane	CH_4	16	-162				65		43			VOLATILE RANGE			
Ethane	C_2H_6	30	-89	-104	-85	-35	79			38					
Propane	C_3H_8	44	-42	-48	-24	12	97		102	93		222			
Butane	C_4H_{10}	60	-1	-5	28	51	100		127						
Pentane	C_5H_{12}	74	36	40	49	81	135		156		141	226			
Hexane	C_6H_{14}	88	69	64	71	120	156		180	141	163	252	80		
Heptane	C_7H_{16}	100	98	95	113	150	176		204		184	258			
Octane	C_8H_{18}	114	125	126	132		194		226	182	216				
Nonane	C_9H_{20}	128	151	149	165		215								
Decane	$C_{10}H_{22}$	142	174	172	184		231							218	
Undecane	$C_{11}H_{24}$	156	196	189											
Dodecane	$C_{12}H_{26}$	170	216				259				SEMI-VOLATILE RANGE				
Tridecane	$C_{13}H_{28}$	184	234												
Tetradecane	$C_{14}H_{30}$	198	253												342
Pentadecane	$C_{15}H_{32}$	212	271												
Hexadecane	$C_{16}H_{34}$	226	288												
Heptadecane	$C_{17}H_{36}$	240	303								NON-VOLATILE RANGE				
Octadecane	$C_{18}H_{38}$	254	317												
Nondecane	$C_{19}H_{40}$	268	350												

TABLE 5
Boiling Points, Pure Compounds (Celsius)
for Organic Toxic Substance Homologues

Figure 3 shows straight and branched chains for the two general classes of organic compounds—aliphatics and aromatics. The C_6 organic compounds are of special interest because they straddle the volatile and semivolatile classifications as shown in Table 5. The aromatic C_6 is important because it represents the parent structure for dioxin-like compounds. It is also one of the more common PICs. The fact that straight versus branched chain distinguishes homologues has relevance in determining separation efficiencies for the more advanced membrane materials. Figure 4 shows the physical arrangement and molecular weight for several semivolatile and nonvolatile compounds of special interest. These compounds are frequently put in one of two synonymous classifications: Polynuclear Aromatics (PNAs) or Polyaromatic Hydrocarbons (PAHs). It should be noted that most of the dioxin-like compounds and many of the nonvolatile compounds which fall within the carcinogen classification have a molecular weight greater than 150. This observation has relevance when membrane separation and containment technology is discussed.

Table 5 also shows the general relationship between volatility (boiling points) and molecular weights. For the same carbon number, the molecular weight for homologues containing one or more inorganic elements will be higher by the differences in the inorganic atomic weight of the replacement element and the hydrogen replacement in the listed paraffin. This table shows the demarcation between volatiles and semivolatiles which has been established previously to be 100°C. Also, the total volatile organic monitoring segment of an EPA Level 1 monitoring system is between C_1-C_6. The molecular weight for octane, C_8H_{18}, is 114. It is clear that most C_8 compounds have a boiling point greater than 100°C, even allowing for highly branched substances. A simplified definition for the separation of the volatile and the semivolatile categories is that volatiles have a molecular weight less than 100, and a boiling point less than 100°C. Some notable exceptions to this rule are the highly chlorinated C_1 and C_2 aliphatics. These compounds have molecular weights in the 118 to 152 range; nevertheless, they fall within the volatile classification. The major reason these constituents fall within the volatile classification is due to the low negative boiling points for the C_1-C_4 paraffins (-1 to -162°C). On balance, the majority of organic substances with a molecular weight greater than 150 will fall within the nonvolatile classification and the semivolatile classification will include substances with a molecular weight range between 100 to 150. The relevance of these observations is of importance to the determination of TOE pathways through the combustion/air pollution control configuration and the selection of membrane separation materials (e.g., when to employ liquid-liquid, liquid-gas, gas-gas separation technology). While the quantities of TOEs present are not relevant for the determination of flow rates, the pathways for the volatile, semivolatile, and nonvolatile TOEs are critical for the determination of the most appropriate containment configurations for organic carcinogens.

In sum, the homologous series concept provides a mechanism to ensure containment of TOEs without knowing which specific compounds are present at any given time. No known single separation technology will contain all TOEs. The critical aspect of containment is that all requisite separation technologies used to contain TOEs should not interfere with the containment of the other PTEs—acid gases, metals, and particulate matter.

There were 98 priority pollutants included in the EPA sponsored industry-wide PIC assessment. Table 6 shows the number of priority pollutants in selected molecular weight ranges and the mass distributions within each volatibility classification.

TABLE 6
Molecular Weight Range vs. Priority Pollutants

Approximate Volatibility Categories	Number of Pollutants	Molecular Weight Range	Percent of Mass Emission
Volatile	29	Less than 100	81
Semivolatile	25 21	100-200 200-300	15
Nonvolatile	18 4 1	300-400 400-500 Greater than 500	4
Total	98		100

Dioxin-like emissions fall within the molecular weight range of 168 to 322. One of the tetrachlorodibenzo-p-dioxin isomers, 2, 3, 7, and 8 TCPD has a boiling point of 447°C, well within the nonvolatile temperature range.

To estimate the amount of these toxic organics in the off-gases which must be contained, one may refer to the two industry wide studies sponsored by the EPA [14]. Both of these documents address PIC emissions from hazardous waste incinerators. Study results [15] were incorporated in part into the later PIC assessment. The earlier report correlates PIC output emissions with POHC input quantities. Both of these studies and other studies used in this assessment correlate the quantity of PIC emissions as a compositional fraction of total gaseous emissions because these data are an integral part of the EPA, Level 1 Monitoring Program.

Neither of these studies correlate the quantities of POHCs destroyed and emitted, the PICs generated and emitted, or the products of complete combustion with the total exhaust gases. These data are necessary to develop an extended flue gas cleaning system that can contain potentially toxic organic materials.The missing component is a mass balance for a representative combustion system. An incinerator design program, developed by ABB Raymond and validated via numerous trial burn results, was used to develop this fundamental mass balance. The requisite results needed to develop the aforementioned relationships are reflected in Table 7.

TABLE 7
Compositional Feed Rate

Input	lbs/hr
Noncombustibles	6,000
Water	3,000
Combustibles	1,000
Total	10,000
Output	
Total Stack Gases	51,353 (13,127 scfm, 180°F)

This compositional feed rate and total exhaust flow rate coupled to the data collected in the previously mentioned EPA sponsored programs provides the mechanism to complete the desired toxic emission containment assessment. The methodology used and results obtained are depicted in subsequent sections.

SYSTEM METHODOLOGY AND DESCRIPTION

This paper shows how toxic emissions can be contained without knowing precisely which toxic emissions are present at any given time. The cleansing and separation of the commingled inert gases are integral parts of toxic emission containment. The separation and cleansing of these inert gases while simultaneously containing all toxic emissions requires an understanding of all the relationships between PTEs, inert gases, and solids undergoing treatment. Further, these relationships must be expressed in absolute rather than relative terms.

Previously, relationships between inert gases and PTEs were derived. Similar relationships for solids and PTEs were also developed. The missing information is the relationship between inert gases and solids. Most of the requisite data discussed previously was on a relative basis as this is the most efficient manner to make comparisons among multiple sites and multiple tests with varying inputs. The relative basis was ppm. In one instance, the comparison media was solids (ash), while in the other, the comparison media was flue gas. None of these data addressed the relationship between the solids and flue gases emitted or the composition of the inert gases in the flue gases despite the fact that about 99.975% of the flue gases are inert gases (nitrogen, water, and carbon dioxide) and the solid fraction of the emissions which can represent about 10% of the total emissions.

To ensure containment of all PTEs, relationships between these classes of variables (PTEs, inert gases, solids) must be developed in absolute rather than relevant terms. The requisite solid relationships are straightforward. The PTE versus the inert gas relationships are more complex because a portion of the requisite separation/containment technologies remove different fractions of these substances. Further, another fraction of these separation/containment technologies remove different quantities within specific PTE subclassifications, particularly organics. Although this fraction of PTEs represents less than .025% of the flue gas throughput, they contain the substances believed to be most detrimental to humans and the environment and therefore, special attention is given to their containment.

While the separation/containment technologies described herein are universally applicable to all combustion devices, a relatively new staged combustion configuration utilizing flue gas recycle with oxygen enhancement is the preferred configuration to minimize the probability of the release of toxic emissions due to operational error or equipment failure. Further, most traditional incinerator configurations can be readily adapted to this mode of operation which is described in detail in the next section. Afterwards, the methodology used to develop the requisite PTE, inert gas, solid relationships on an absolute basis is presented. Only then is it possible to address the separation and cleansing of inert gases while containing toxic emissions.

Flue Gas Recycle Versus Traditional Thermal Treatment

The generation of off-gases containing potentially toxic combustion by-products is reduced by 80% whenever a flue gas recycle configuration, coupled with the utilization of oxygen as the oxidant, is employed. For this reason, this configuration is used as the basis for developing the aforementioned relationships between PTEs and inert gas pathways. The utilization of other combustion flue gas cleaning systems without the utilization of flue gas recycle or pure oxygen will affect the sizing of intermediate unit operations (subcooling and absorption). The higher gas flows will have a less pronounced impact when sizing any of the requisite membrane configurations. Regardless, the PTEs containment results will be similar to those presented at this time.

Figure 5 shows a simplified general arrangement schematic of the proposed system which is comprised of six major subsystems: 1) oxidation; 2) vitrification; 3) flue gas cleaning; 4) subcooling; 5) absorption; and 6) membrane configurations. The schematic emphasizes the novel use of proven technologies (membranes and absorption) and the interfaces between the novel and the more traditional incineration technologies. There have been many facets of this configuration reported in the literature [16; 17; 18; 19; 20; 21]. In addition to the 80% total off-gas reduction, about 60% of the effluent is recycled for further treatment. This recycle automatically doubles the thermal treatment time for 60% of the PTEs, thereby ensuring a significant reduction of PTEs entering the extended flue gas cleaning system.

The purpose of the thermal oxidizer is to separate the waste constituents which volatize below 1400°F before subjecting the residuals to higher temperatures in the vitrification unit. The majority of the constituents which volatize below 1400°F fall into two categories—water (aqueous solutions) and organics. It is imperative that these substances be removed before the residuals are subjected to higher temperatures in the vitrifier as the volumes of these volatiles will increase about 5000% over their volumes at ambient temperatures. It should also be noted that some fission product forms (e.g., Ru, Cs, Tc, and I) will volatize at these temperatures. Any ^{14}C and tritium will also volatize as CO_2 and H_2O, respectively. The rapid expansion of these substances can result in detrimental chemical reactions in the vitrification process or in the unit operations downstream of the vitrification unit.

During normal operations, the residual inert material transverses the kiln in 40 minutes and exits the kiln at a temperature 200°F less than the gas exit temperature. A minimum kiln residual temperature of 1200°F is required to ensure that organic volatiles are not present in all types of residuals. In the recommended configuration, the kiln residuals drop directly into a vitrification furnace, which also accepts admixtures, and can operate at any desired temperature less than 3000°F. Normally, vitrification temperatures fall between 2300°F and 2500°F. These temperatures are adequate to decompose the 10 ppm to 2000 ppm of organic residuals and bond the 365 ppm to 45,000 ppm of metals with the admixtures and ash minerals, thus containment of these potentially toxic emissions is assured. Higher temperatures are normally used in metal refining. Admixtures may be used in either vitrification or metal refining. The technical feature that distinguishes metal refining from vitrification is that nearly all the solids must be liquified to achieve the metal segregation that occurs by differences in specific gravity whenever the thermal reactor residence time is sufficient to allow stratification after liquefaction.

There is a seal between the vitrifier and the kiln discharge breaching. Since the kiln discharge breaching is always under negative pressure, the vapors generated during vitrification will flow directly into the secondary combustion chamber and mix with the kiln off-gases prior to being subjected to further treatment. The vitrifier vapor flow will not be significant. It represents less than 5% of the kiln off-gases. The primary substance classification of the vitrifier off-gases will be inorganic molecules, compounds, and/or complexes. The retrofitting of the vitrifier to an existing incinerator system should not cause the incinerator to be down rated from a throughput viewpoint. Volatization of some fission products in this stream is likely. Ruthenium, cesium, technetium, and iodine are volatile. Other radionuclides will be carried in the gas stream sorbed on fine particles contained in the flue gas. The kiln and vitrifier off-gases flow into the second-stage thermal oxidizer where the gas/vapor temperature is elevated to between 1800°F and 2200°F in the presence of excess oxygen to reduce the residual organics to CO_2 and water. If required, fuel will be added to achieve the desired operating temperature.

For the purpose of this paper, a combination type APCS is assumed. In this arrangement, the flue gases will be quenched to the appropriate temperature levels prior to particulate removal and neutralization. As the gas cools, cesium and technetium salts will drop out of the gas as solids. Much of the ruthenium and iodine will be held up in the caustic wash. After the particulate is removed, it will be briquetted and inserted directly into the vitrifier. Most of the radionuclides that exit the combustor will be associated with this particulate matter. The blowdown from the neutralization process can be reintroduced into the process with the quench water. If large quantities of solids are present, filtration may be required prior to mixing with the quench water. The solid residues will be inserted into the vitrifier and converted into a stabilized waste form..

There are several other flue gas cleaning configurations which are capable of producing the removal efficiencies used in this study. Should these configurations not be capable of operating in a closed loop manner similar to the one described, the open stream(s) can be integrated into the proposed extended flue gas cleaning system, if required. The draft *Combustion Emissions Technical Resource Document* depicts cumulative distributions of the HWI PM. This type of industry wide data, from multiple APCSs, was used in this study. The sizing of the PTE containment equipment is not sensitive to these minute quantities; the relevant issue is the assurance that these constituents can be contained.

Feedstock Quantities and Composition

With the processing configuration defined, the relationships between flue gases, PTEs, and ash can be determined for a particular feedrate and composition. The feedrate is the primary variable for size determination. For the stated objectives, feedstock composition is more important in determining the desired relationships and for determining the component pathways through the configuration. The representative compositional feedrates used are reflected in Table 8. Table 8 contains the precursor quantities necessary to determine all major PTE quantities and inert gas classification quantities and the ensuing pathways through the entire processing configuration.

TABLE 8
PTE Compositional Feed Rates

Feed Category	Feed Rate lb/hr
Solids	
Halogens	500
Sulfur	50
Nitrogen	25
Metals	350
Inerts	5,075
Subtotal	6,000
Water	3,000
Organics	1,000
Total	10,000

Quantification of Inert Gas Compositions and Pathways

Heat and material balances for the inert gases and PTEs were calculated and reported previously [22]. Figure 6 shows the inert gas pathways through this system depicting three types of separation technologies: subcooling, absorption, membranes. Only one membrane system is reflected as there is only one major inert gas separation. The membrane retentate, Node 5, plus the primary recycle, Node 3, represents the sum of the inert flue gases recycled. The water removed from the flue gas in the condenser and the absorber is also recycled. These data are summarized in Table 9. This table also compares the inert gas emissions with the similar emissions from a traditional incinerator configuration.

TABLE 9
Inert Gas Mass Balance
(Contained vs. Emitted)

Category	Disposition				Total	
	Recycled		Emitted			
	lbs/hr	%	lbs/hr	%	lbs/hr	%
Primary recycle	18, 945	36.9				
Condenser water	4,356	8.5				
Absorption gases	966	1.9	1,823	3.5		
Regenerator gases			5,003	9.7		
Absorption water	93	.2				
Subtotal	24,360	47.5	6,826	13.2	31,186	60.7
Combustion with oxygen reduction					20,167	39.3
Grand Total (Traditional Configuration)					51,353	100

Table 9 shows that only 13.2% of the flue gases generated with conventual combustion practices are emitted in the proposed system. The remaining 86.8% of the conventual flue gases generated are either recycled or eliminated due to the use of oxygen instead of air as an oxidizer. The retentate from the extended flue gas cleaning system (three streams) are either recycled back to the combustion system or the APCS and represents 10.6% of the flue gases emitted from a traditional configuration. Oxygen enrichment (the elimination of nitrogen) accounts for 39.3% of the flue gases emitted from a traditional configuration. The primary recycle, used to reduce the flame temperature in lieu of nitrogen in one of the combustion chambers, represents 36.9% of the flue gases emitted from the traditional system. More importantly, approximately 60% of the flue gases generated in the closed loop configuration are automatically recycled before entering the extended flue gas cleaning system; therefore, the impact from unplanned transient flow rates are significantly dampened by the closed loop recycling of off-gases. A further dampening effect occurs when about 40% of the off-gases entering the extended flue gas cleaning system are also recycled. The combination of these various recycling stages coupled to the unique separation characteristics of the selected membranes assures containment of toxic emissions, prior to the last possible recycling stage used to return contaminated inert gas products prior to release.

PTE Pathways and Control

The quantities of PTEs leaving the outlet of a traditional hazardous waste incinerator configuration are summarized in the section entitled "Definition and Significance of Potentially Toxic Combustion By-products". These data are all reported on an incremental basis ppm as contrasted by the data shown in Figure 6. These data reflect the inert gas mass balance for the extended flue gas cleaning system which, when coupled with the proposed recycle schemes, is capable of containing all PTEs or cleaning them to a specified limit prior to emitting them to the environment.

Figure 6 shows the separation technology flow sequence to be subcooling, absorption, stripping, and membranes. The primary objective for using subcooling and absorption is to remove inert gases—subcooling removes water vapor and absorption removes carbon dioxide. Both of these unit operations will remove a fraction of PTEs as well. Before the liquid effluent from either of these unit operations is reused or recycled elsewhere in the process, further treatment may be required. If so, membrane technology is the most likely separation process to be used. Whether further treatment is required is primarily a function of feedstock composition, the efficiency of the existing air pollution control system and the manner in which the combustion subsystem is operated. All of these potential membrane applications do not appear in Figure 7 since they are considered to be optional unit operations. These optional unit operations are discussed in the subsequent section which focuses on membrane applications.

Subcooling

The purpose of this unit operation is to remove the water from the flue gas. Most flue gas emissions leaving a BDAT air pollution control system are saturated at a temperature between 160°F to 180°F depending upon ambient temperatures. When these flue gases are cooled from 180°F to 100°F, the water content drops from 38% to 4% of the flue gas flow rate. For the given example, 4356 lbs/hr of water is condensed. By condensing this water, the air emissions are reduced 8.5%. Further, this water can be readily recycled to the quench tank, usually the first unit operation in the APCS configuration. More importantly, some 59% of the potentially toxic emissions will probably be removed with the water. A fraction of the PTEs removed are chemically or physically bound with the water. Another fraction of PTEs become encapsulated when the water condenses. A portion of the semivolatile PTEs condenses naturally when the temperature is lowered 80°F. Depending upon the class and quantities of potentially toxic emissions present in the water, a membrane configuration may be required to prevent metal accumulation when the water is directly recycled. Should excessive quantities of potentially toxic metals be present, the fraction of the condensate containing the metals will be processed further in the vitrifier.

Table 10 complements the inert gas mass balance reflected in the Simplified Chemical Absorption Flow Schematic. The quantities and compositions are summarized from the material presented in Table 10.

TABLE 10
Condenser: Potentially Toxic Emission Mass Balance
(PPM Mass)

Constituent	Input	Water Outlet	Vapor Outlet
Halogens	100	50	50
Sulfur	100	50	50
Nitrogen	500		500
Inorganic metals	1000	900	100
Hydrocarbons			
Volatile	8	2	6
Semivolatile	4	4	0
Nonvolatile	1	1	0
Particulate matter	39	20	19
Totals	1752	1027	725

The removal of 50% of the halogens and the sulfur constituents is believed to be conservative as the majority of these substances are soluble in water and have low vapor pressures. Most of the residual nitrogen, if present, will probably be in the form of NO which has a very low solubility; therefore, it will remain in the gas/vapor phase. Most of the inorganic metals will be removed with the water as most are reasonably soluble or have low vapor pressures. The particulate matter is considered to be submicron inert mineral matter. The most likely capture mechanism is encapsulation. This capture mechanism will also enhance the removal of heavy metals and nonvolatile organics.

Table 10 shows that 1027 ppm of potentially toxic substances are present in 4356 lbs/hr (523 gal/hr) of condensed water. With the exception of the 7 ppm of hydrocarbon constituents, these substances could readily be returned to the APCS since the APCS accessories are already designed to process these materials. It should be noted that up to 5 ppm of these hydrocarbon substances are in the semivolatile and nonvolatile categories. These categories may contain dioxin-like compounds. Should it be necessary to treat this waste stream, approximately 90% of this water could be purified by the utilization of membrane technology similar to reverse osmosis systems used to provide drinking water throughout the world. Over 90% (834 ppm) of the inorganic metals, the hydrocarbons, and the particulate matter would remain in the retentate. Up to 193 ppm would remain with the purified water which could then be recycled to the quench tank of the APCS. The remaining 653 lb/hr of water containing some 834 ppm of potentially toxic substances could be compacted with admixtures and returned to the vitrifier.

Absorption Technology

The purpose of this configuration is to remove and clean the carbon dioxide prior to release. The amount of carbon dioxide present represents 73% of the remaining flue gases to be released from the system.

Theoretically, membranes could also be used to make this separation at a reduced cost; however, since this is the primary stream to be released, special attention is given to ensure effective cleaning during transient operating conditions. The absorption process requires two phase changes; therefore, more effective separation is anticipated. During the liquid processing phase, adequate hold up time is available for sampling and analysis. Special provisions have been made to reprocess off-specification material. This intermittent recycling step is not reflected on the subject schematics.

Table 11 shows the anticipated partitioning of substances being processed in the tower. The gas stream outlet is the input stream to the membrane configuration shown in Figure 6. The separation and cleaning of these flue gases is addressed in the next section.

The potentially toxic emissions in the liquid stream will probably remain in the liquid stream during the regeneration (regasification) of the carbon dioxide. This intermittent cleansing step is not reflected on the simplified flow schematic. Chemical precipitation, crystallization, or membrane technology can be used to make the requisite separations prior to recycling the residues to the vitrifier and the cleaned absorbent back to the absorption tower.

TABLE 11
Absorption Tower: Potentially Toxic Emission Mass Balance
(PPM mass)

Constituents	Inlet Vapor Stream	Outlet Gas Stream	Liquid Stream
Halogens	50	1	49
Sulfur	50	1	49
Nitrogen (NO)	500	500	0
Metals	100	25	75
Volatile organics	6	6	0
Particulate matter	19	5	14
Total	725	538	187

Figure 5 shows two other inexpensive cleaning options. After the sampling and analysis hold-up tank, there is a stripper that is used to remove potentially toxic substances which are more volatile than carbon dioxide should they still be present at this point in the process. A membrane configuration may be installed in-line to separate semivolatile materials with permeation rates different than carbon dioxide after the carbon dioxide regeneration column.

With all the available cleaning options, it is reasonable to believe that less than 1 ppm of potentially toxic substances will be released with the carbon dioxide and that none of these emissions will be dioxin-like organic materials.

Membrane Technology

The primary reason for utilizing subcooling and absorption in the extended flue gas cleaning system was to remove the water vapor and carbon dioxide from the flue gases. This was necessary to enhance the operation of the membrane separation technology which also serves to contain (prevent the release of) PTEs, especially those with a molecular weight greater than 100. A secondary reason for utilizing membrane technology is to separate and recycle the "excess oxygen" in the flue gases. Different types of membrane materials and configurations are required to remove different classes of PTEs. There is more commonality relative to the use of membrane configuration technology than there is with the manufacture of membrane materials. The following discussion of membrane technologies emphasizes the more common aspects of membrane configurations which can be adapted for use in the extended flue gas cleaning system. Significant differences relative to the most appropriate types of membrane materials applicable to specific classes of PTEs will be noted.

The commercial development of membrane technology extends beyond 50 years. Over time, membrane technology has been subdivided into five subcategories. Figure 7 shows the relationship between particulate matter particle size, various units of measure and the effective process classification separation range. Of special interest is that molecular weight has been introduced as a unit of measurement. A molecular weight of 200 is equivalent to 10 angstroms, 0.001 microns, 1 nanometer. Most potentially toxic metals and organics have a molecular weight less than 200. Some organic and metal specie of interest fall within a molecular weight range of 25 to 50.

All particulate matter of interest are present in sizes less than 2 microns; most are present in sizes less than 0.01 microns. This particle size range coincides with all membrane technology classifications.

A summary of these applications is presented in Table 12. Microfiltration and ultrafiltration focus on solid-liquid separation, hyperfiltration (reverse osmosis) provides liquid-liquid and liquid-gas extraction while gas permeation deals with gas-gas separation. The overall membrane pore size ranges from 2A to 2 microns. All of these membrane technology classifications may be used in the proposed extended flue gas cleaning system.

From a toxic combustion by-product viewpoint, microfiltration and ultrafiltration membranes can be used to remove rogue particulate matter as well as nonvolatile and semivolatile organics present in the form of colloids and emulsions. Reverse osmosis membranes can be used to remove soluble inorganic metals and most organic compounds with a molecular weight greater than 100. Porous gas permeation membranes, the type membranes reflected in Table 12, can be used to separate residual gases; however, this mechanism is quite limited due to the low separation factors that can be achieved with this type membrane material. It should be noted that there is overlap in the pore size ranges between ultrafiltration, hyperfiltration and gas permeation. The pore size range for ultrafiltration is between 10Å-1000Å. Ultrafiltration membranes are capable of removing most nonvolatile organics. The pore size range of hyperfiltration is 5Å-20Å. This class of membranes will remove most semivolatile hydrocarbons and inorganic metal contaminants. To achieve effective separation of volatile "organic" and nonorganic gases, the membrane pores should be less than 10Å.

For the stated objectives, it is sufficient to recognize that there are three different types of membranes available: porous, nonporous (dense phase), and coupled transport. Coupled transport, also called liquid membranes, can be viewed as an extension of the dense phase membranes. During the last decade, many of the major development activities have been in the area of dense phase membranes. As the terms suggest, these membranes do not have pores in the conventional sense. The gases are instead separated on the basis of their solubility in, and diffusivity through, the membrane material. Many of the early applications were directed toward the hydrocarbon processing industries for the recovery of hydrogen, carbon dioxide, C_1-C_6 aliphatics and C_6-C_8 aromatics [23]. Some of these systems were installed in the late 1970s. There are currently numerous applications throughout the hydrocarbon processing industry with gas throughputs 5 to 20 times the gas throughputs required for most industrial combustion systems. It was reported that one of these systems rated at 20×10^6 SCFD (13,888 scfm) was placed on a module 9' wide x 9' high x 12' long [24].

In sum, the more recent membrane technology developments focused on the manufacture of the membrane material with most current developments addressing the separation of the lighter gases (N_2, O_2, etc.) Another new development of interest is the extended recovery of hydrocarbons previously hampered by premature condensation of heavier (semivolatile) hydrocarbons on the membrane surface due to the depletion of lighter gases in the retentate [25]. Of special interest, especially when processing nuclear wastes, are the development activities associated with liquid membranes, which were first created in 1968 [26]. Liquid membranes consist of a contained liquid between two membranes. The permeate must be transferred across both membranes. The contained liquid facilitates the transport without a permanent physical or chemical change in makeup. An analogy can be seen with hemoglobin in the blood. Hemoglobin is a transport liquid which circulates through the body delivering oxygen through the blood vessels from the lungs to the terminal tissues. It is not possible for the hemoglobin to diffuse across the membranes because it is too bulky with a nominal molecular weight of 65,000. A more complete discussion on liquid membranes is available in various sources [27; 28]. The two potential usage areas are 1) the enhanced separation of oxygen, nitrogen and volatile organics; and 2) specie-specific removal for secondary waste reduction, especially radioactive metals.

TABLE 12
Crossflow Separation Processes*

Application	Membrane Pore Size	Fluid Components Retained	Transmembrane Pressure (Typical)	Sample Applications
Microfiltration	0.1μm-2μm	Very small suspended particles, some emulsions, most bacteria	1 psig (7 kPa) 25 psig (172 kPa)	High volume removal of bacteria and small suspended solids; eliminate frequent filter changeouts, extend life of point-of-use submicron filters in ultrapure water applications; beverage clarification.
Ultrafiltration	10Å-0.1μm	Most organics over 1000 MW, including pyrogens, viruses, bacteria, colloids	10 psig (69 kPa)- 200 psig (1380 kPa)	Pre and post treatment to Ion Exchange; fractionation and concentration of proteins, blood, foodstuffs, vegetable extracts; purification and clarification of fermentation broths; concentration and recovery of industrial organics and dilute suspended oils.
Reverse osmosis (Hyperfiltration)	5Å-20Å	Ions and most organics over 100 molecular weight (MW)	200 psig (1380 kPa) 1000 psig (6890 kPa)	Brackish and seawater desalting; pre- and post-treatment to ion exchange; metal ion recovery; sugar concentration; boiler feed purification; BOD and COD reduction in waste streams.
Gas permeation	2Å-50Å	Gases with relatively low permeability through the membrane polymer, particles in gas, vapors in gas	Vacuum to 2000 psig (13,800 kPa)	Separate and/or purify mixed gas streams, "sweeten" sour natural gas; CO_2 recovery and enrichment in enhanced oil recovery; generate O_2 enriched air for medical and combustion uses; dry gases.

* Osmonics Technical Literature

Most of the commercialization of gas-gas separation has occurred over the last 20 years. Technical advances during the last decade have increased some types of gas separation efficiencies 200-400% [29]. This rapid growth rate makes technical and economic comparison difficult. Another comparison complexity arises because many membrane separation processes do not neatly replace existing separation processes, but rather complement them, a fact especially true in the extended flue gas cleaning system. In general, membrane configurations are very flexible, require low capital investment, are easy to operate with low energy consumption, are cost-effective even at low gas volumes, and have good weight and space efficiency [30]. Separation is achieved by correlating the particle size and/or molecular weight of the substance to be removed with the pore size in the membrane. Figure 7 correlates the membrane technology categories with the particle size ranges for various types of substances defined and quantified in the previous section.

This simple correlation is effective when the particle size is greater than 10 angstroms (1 nanometer, a molecular weight greater than 200). Here the focus is on volatile combustion by-products leaving the absorption tower. These by-products will have a molecular weight less than 100 (less than 4 angstroms). Many of the combustion by-products will have a molecular weight less than 50. In this particle size range two other parameters, and solubility are also controlling permeation. The membranes used in this gas-gas separation range are referred to as nonporous or dense phase membranes since they are not manufactured according to precise pore size specifications. Table 13 presents an overview of the requisite separation information for dense phase membrane permeation materials.

TABLE 13
Relative Gas Permeation Rates vs. Molecular Weight*
for
Dense Phase Membrane Material

Categories	Constituent	Relative Permeation Rate	Molecular Weight
1	Water vapor	100	18
	Hydrogen	12	2
	Carbon dioxide	6	44
	Oxygen	1	32
2	Carbon monoxide	.3	28
	Methane	.2	16
	Nitrogen oxide	-	30
	Nitrogen	.18	28
	Ethane	.10	30
3	Propane	less than .10	44
	Halogenated hydrocarbons	less than .10	more than 50
	Oxygenated hydrocarbons	less than .10	more than 50

* [31]

This table does not show any metal data. Most metal substances will have a molecular weight greater than 50 and will fall in Category 3, a class of compounds which can be relatively easily separated at or above the 90% removal rate by a nondense (porous) membrane material. Reverse osmosis, using a porous membrane material, has been used successfully to separate soluble metals for over 20 years. Lithium, beryllium, and boron are potential exceptions, depending primarily upon the substance forming the chemical bond.

It should also be noted that organic gases comprised of more than three carbon elements have very low permeation rates when compared to the other major flue gas components (e.g., water vapor, CO_2, O_2, CO, CH_4, C_1s, etc.). Porous membranes are normally used to separate specie which contain more than three carbon elements. Note: Should these specie be present in trace amounts and are not separated prior to entering a dense phase membrane system, they will be contained and may condense after the major constituents have permeated the membrane. Should this occur, the membrane will not be significantly damaged and provisions can be made to remove the condensation [32; 33]. It has been reported that there was only a 20% membrane deterioration over a 2-year period when processing the gas composition depicted in Table 14 [34]. Membrane deterioration is normally anticipated in configuration designs; therefore, membrane replacement is not a significant off-stream consideration.

TABLE 14
CO_2 Recovery by Gas Permeation
Typical Examples of Acid Gas and Hydrocarbon Feedstock Composition
(Mol %)

Constituent	Example 1*	Example 2**
CO_2	47.5	15.01
N_2		2.68
H_2S		.06
C_1s		73.89
C_2s	21.8	5.03
C_3s	18.8	1.79
i C_4s	2.2	.34
n C_4s	5.8	.55
i C_5s	1.4	.19
n C_5s	1.2	.18
C_6s	.8	.13
C_7^+s		.15
TOTALS	99.5	100.00

*[35]
**[36]

These data reflect volatile and semivolatile organic concentrations well above those expected in the flue gases of a combustion system, even under upset conditions. Given the fact that many of these gas separation systems have been in operation over 15 years at gas flow rates 5 to 20 times the flow and organic concentration rates developed in most industrial combustion systems, membrane technology should be considered a proven technology despite the fact that none are currently operating in the mode of an extended flue gas cleaning system for an industrial combustion application.

In general, membrane configurations, regardless of the material utilized in the manufacturing process can operate effectively within the operating ranges shown in Table 15. Inducing a vacuum on the downstream side of a membrane can provide effective permeation at a lower inlet pressure.

TABLE 15
Operating Ranges for Membrane Configurations*

Processing Variable	Operating Range
Pressure	200 psig to 2000 psig differential
Temperature	100°F to 195°F
Water vapor	Saturated or 20°F-50°F above dewpoint
CO_2	0%-90%
Organics	
Paraffins	Condensation points must be 20°F above dewpoint
Olefins	25% of saturation
Aromatics	10% of saturation

* [37]; [38]; [39]

Membrane Process Configurations

Although there are frequent improvements relative to the composition and manufacturing techniques associated with membrane material, the manner in which the membrane material is incorporated into the process configuration has been relatively consistent over the last two decades. Typically, the membrane material is spirally wrapped around a porous discharge pipe (2-ft to 6-ft long) and inserted into a larger diameter (4 in to 12 in) cylinder. On occasion, the outside containment cylinder may contain more than one spirally wrapped bundle. For a given feedstock and product composition, operating temperature and pressure, and membrane material, the amount of membrane surface area required can be determined in a straightforward manner. Operating flexibility and feedstock variations determine to a large extent the measure in which the most appropriate process is configured. Several examples are cited.

Figure 8A shows that the feedstock is divided into two streams: the permeate is the feedstock passing through the membrane; the retentate (residue) is that fraction of feedstock which is retained by the membrane. Normally, particulate matter, metals, nonvolatile and semivolatile organics will remain in the retentate while the recyclable volatile organics may be in either the permeate or retentate depending upon the membrane material selected.

Figure 8B shows three forms of complexity. First, multiple stages are frequently used because it is not always possible to obtain the desired concentrations in both the permeate and retentate streams in a single stage unless there is a significant difference in the molecular weight of the substances to be separated. Second, it is not necessary to use the same membrane material in both stages. Third, recycling can be used to enhance the separation factor. Either the permeate or the retentate can be recycled. In either situation, recycling enhances separation when process flows fall below normal. Conversely, higher than normal flows will not produce deleterious separation factors unless these higher flow rates prevail over an extended period.

Figure 8C provides the greatest operating flexibility for minimum incremental costs. Figure 8C shows two retentate and one permeate effluent. It is obvious that, with minor piping modifications, it is possible to obtain one retentate and two permeate effluents. Any one of these streams can be fed forward or backward in the process. There usually are less cylinders in the downstream stages since substances are being withdrawn between stages. The major advantage of having multiple cylinders in the same stage is that tube bundle segments which have deteriorated can be replaced without taking the entire configuration offstream. Normally, it is possible to isolate individual cylinders within a given stage to remove the damaged tube bundle. Usually the tube bundles near the discharge are most susceptible to damage. The resulting temporary increase in flow to the other cylinders in the stage will not significantly reduce product quality. At times when the feedstock is unusually dirty, backwash and chemical treatment systems are included to refurbish individual or multiple cylinders in the configuration. Recycle lines can be incorporated into this design.

The previous examples were selected to show the manner in which membrane technology could be used to effectively contain all PTEs by complementing existing equipment and to demonstrate the operating flexibility for separating particles being transported in either a gas or liquid media and where the particles are less than 2 microns with emphasis or particles less than 50 A°. The evolution of membrane development has resulted in what appears to be the application of five distinct technologies whereas Figure 7 shows these technologies to lay on a continuous spectrum of particle sizes between 5 A° to 2 microns with the recent technology development activities occurring with the separation of smaller and smaller particles. The most recent technology development has occurred in the manner in which the membrane materials are manufactured. The method for constructing the modules used in the field has been relatively consistent over time. For this reason, particle size distribution and concentration levels are the critical design parameters when utilizing membrane technology.

Figure 5 shows three potential membrane applications. Two applications involve separating solids from gas media (gas-gas separation); the absorber and regenerator off-gas streams. The other application involves solid-liquid separation; the subcooler condensate and the optional intermittent solid-liquid separation unit on the absorbent recycle line which is not shown. The absorber off-gas membrane configuration will require two or more stages due to the similarity in gas permeation rates (See Categories 1 and 2, Table 6). The other applications should not require more than two stages unless there are unusually high concentrations of acid gases, metals, or nonvolatile organics present.

Analysis of Emissions Prior to Release

All emissions will be analyzed prior to release. The same methodology will be used for both carbon dioxide and nitrogen gaseous emission steams. Parallel holding tanks in the storage area will be used sequentially. Analysis time requirements are six minutes for organics and any single or multiple volatile contaminate(s) can be used to specify release specifications. When radionuclides are present, the gases will be released from the system only after they have been held long enough to assure no radionuclides are present (or more precisely, below release limits). The holdup time will be a function of the radioactive release criteria; the lower the limits, the longer will be the holdup (counting) time. Analysis for radionuclides will be done by alpha and beta/gamma counting. The analysis time will be inversely proportional to sample volume. The lower the required release limits, the longer the analysis time will be.

During the 1980s, the weakest technical link in establishing NESHAP standards for organic priority pollutants was the ability to accurately measure these pollutants continuously. The instrument most frequently used was the Flame Ionization Detector, also referred to as a total hydrocarbon analyzer. As a result of several major programs sponsored by EPA during the 1980s, utilizing complex sampling techniques and different analysis methodologies, several organic substances have been identified to be good indicators of the generation of organic PTEs [40; 41]. The substances most frequently found were C_1s and C_2s. Benzene was the exception. The predictive substances had varying degrees of halogen saturation. Typical examples were: methane, ethane, ethylene, methylene chloride, chloroform, carbon tetrachloride, tri and tetra chlorothylene, chlorobenzene. Within the last five years, new instrumentation coupled with computer software programs have significantly enhanced the analysis of volatile PTEs. One example is the Fourier Transform Infrared (FTIR) spectrometer system developed by Argonne National Laboratory. This system automatically follows a procedure being evaluated by the EPA Office of Air Quality Planning and Standards for compliance. It should be noted that the FTIR is also capable of analyzing for inorganic atmospheric gases such as SO_2, NO_x, CO, CO_2, NH_3, HCl. It should be also noted that, in 1993, the Texas Air Control Board allowed the utilization of a predictive emissions monitoring system to comply with the CAAA. Clearly the utilization of these analytic tools in conjunction with the aforementioned separation technologies ensures containment of all toxic emissions.

SUMMARY

The focus of this paper was on the generation, control, and containment of potentially toxic combustion by-products. An approach was advanced which would enable one to overcome the existing effluent measurement dilemma, especially the organic emissions which cannot be precisely quantified. Emphasis was given to organic emissions because this category of toxic emissions is perceived to be the most harmful to humans and the environment.

The results presented in this paper were integrated into another paper presented elsewhere [22]. In sum, the other less complex toxic emission categories were subjected to the same analytic methodology used in this paper to define and quantify organic emissions. The results from this integrated assessment are summarized here for completeness.

1. The total gaseous emissions from the recyclable extended flue gas cleaning system are 13.3% of the total gaseous emissions from a BDAT configuration.
2. There are 10 ppm to 2000 ppm organic and 365 ppm to 44,763 ppm metal priority pollutants in the bottom ash of BDAT incinerators. These potentially toxic substances will either be removed or chemically bonded to contain these substances within the residues.
3. There are about 200 ppm of acid gas constituents leaving a BDAT incinerator. This value will be reduced to 2 ppm in the recyclable configuration.
4. There are 39 ppm of particulate matter leaving a BDAT incinerator. This value will be reduced to 1 ppm in a recyclable configuration.
5. There may be 5 ppm of semivolatile and nonvolatile potentially toxic organic compounds, including dioxin-like emissions, leaving a BDAT incinerator, which will be contained in a recyclable configuration.
6. There may be 8 ppm of volatile organic emissions leaving a BDAT incinerator. If so, 6 ppm (75%) of these constituents will be contained in a recyclable configuration.

CONCLUSIONS

The combined results from this integrated assessment demonstrate that it is possible to use proven technology to contain the potentially toxic emissions generated during the combustion of organic materials even if the precise quantities of potentially toxic emissions are not known and cannot be continuously measured online in real time.

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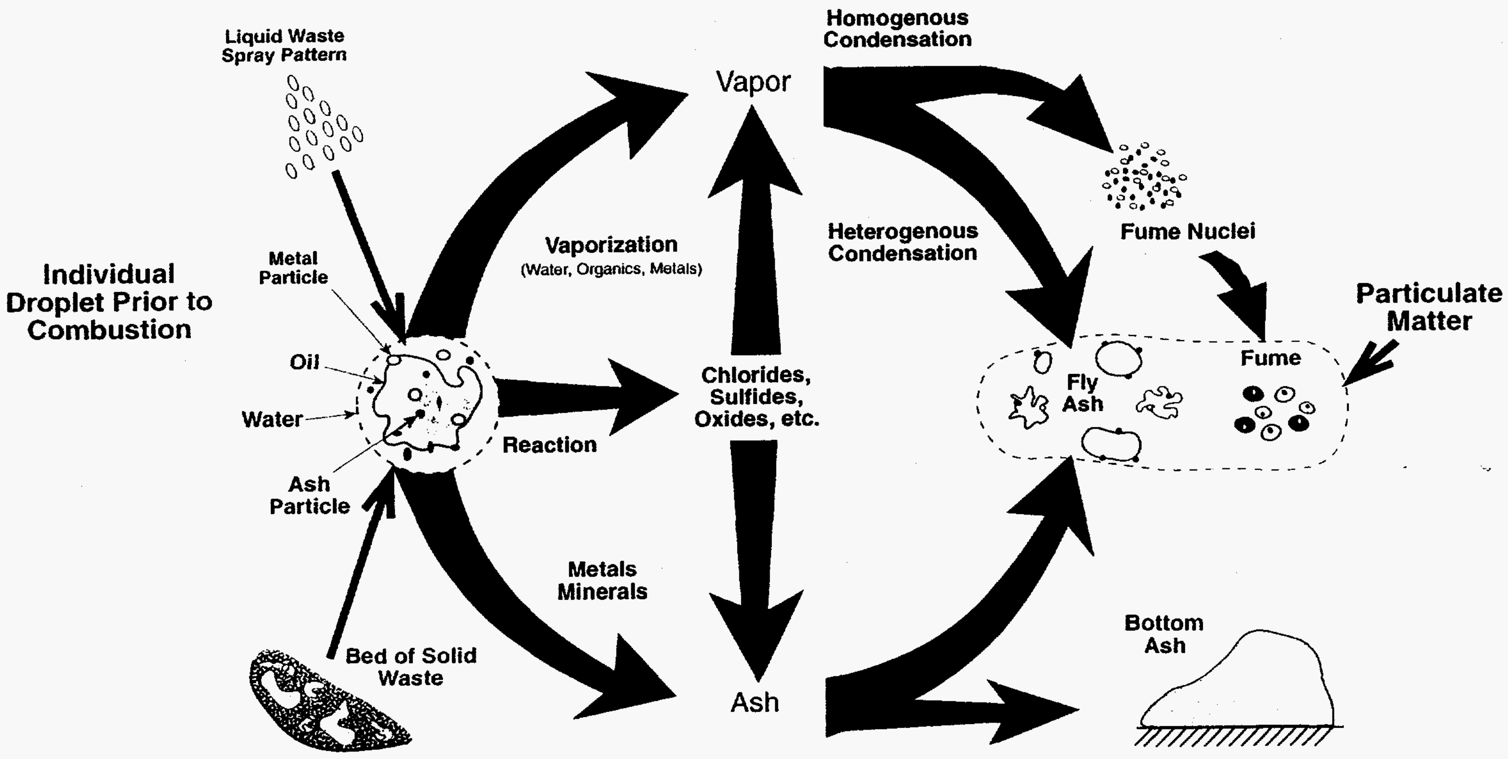
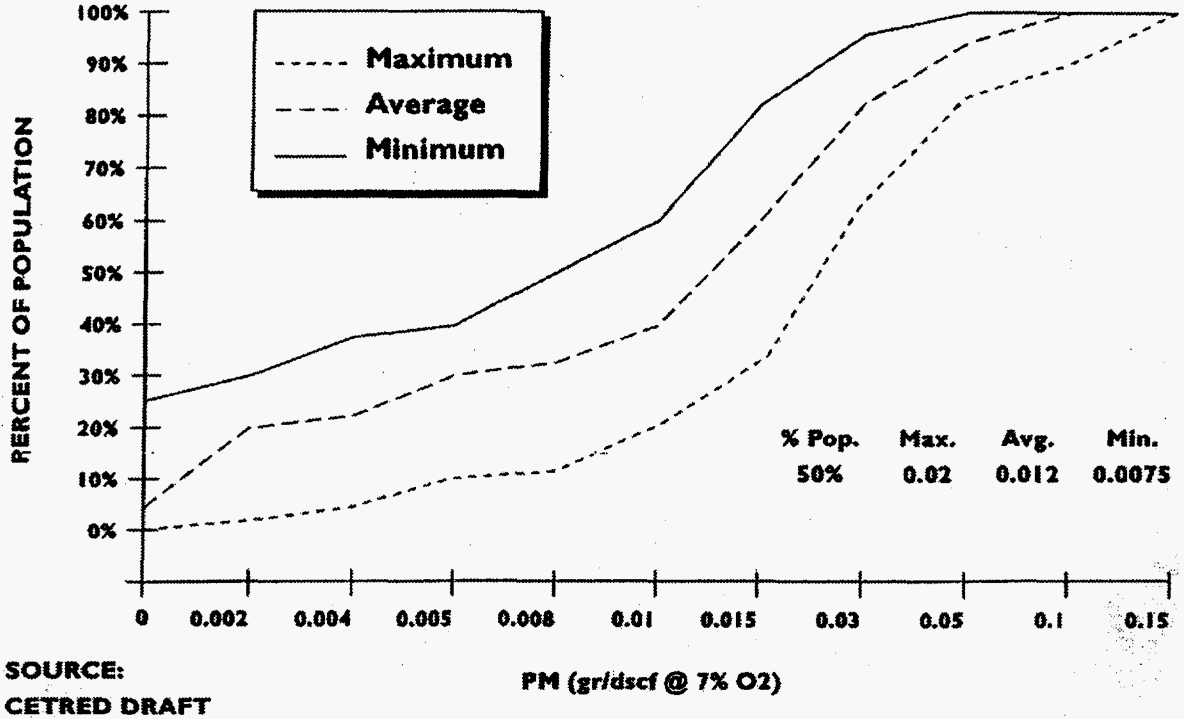


FIGURE 1
Generation Mechanisms for Toxic Substances



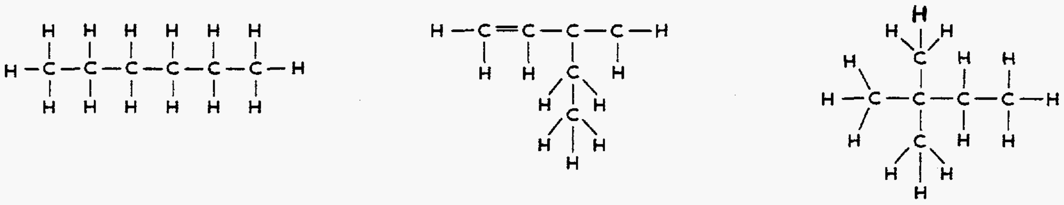
SOURCE:
CETRED DRAFT

FIGURE 2
Cumulative Distribution of HWI PM Emissions

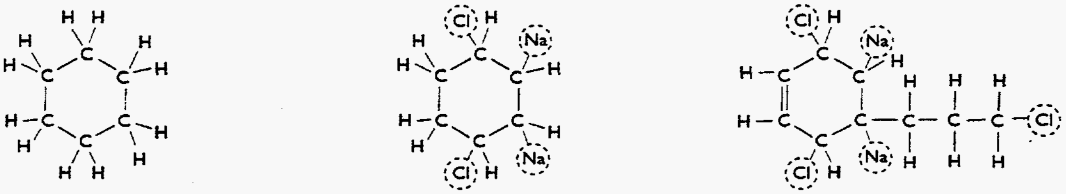
ALIPHATICS

STRAIGHT CHAIN ARRANGEMENT

BRANCHED CHAIN ARRANGEMENTS



CYCLO (RING) ARRANGEMENTS



AROMATICS

BASIC STRUCTURE

TOLUENE

DI-ETHYL PHTHALATE

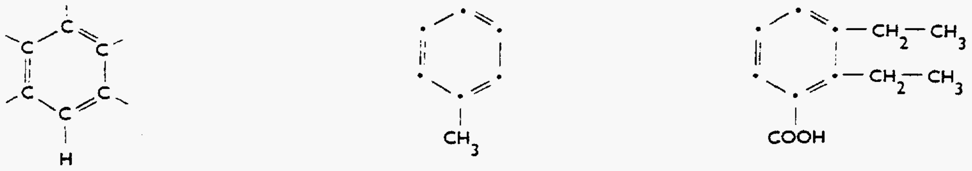
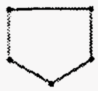


FIGURE 3
Representative Physical Structures
of Typical C_6 Priority Pollutants

CYCLOPENTADIENE



C_5H_{10}

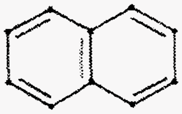
(70)[2]

BENZENE

C_6H_6

(78)

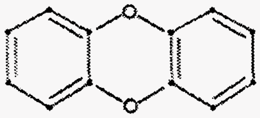
NAPHTHALENE



$C_{10}H_8$

(128)

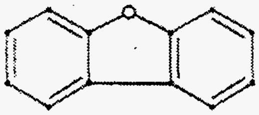
DIOXINS



$C_{12}H_8O_2$

(184)

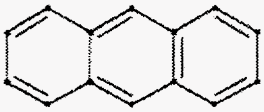
FURANS



$C_{12}H_8O$

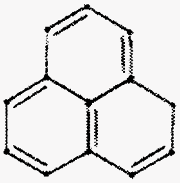
(168)

ANTHRACENES



$C_{14}H_{10}$

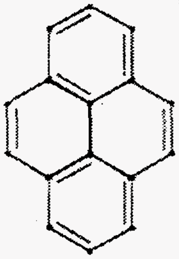
(178)



$C_{14}H_{10}$

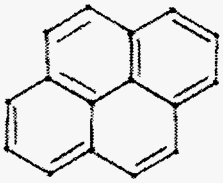
(178)

PYRENES



$C_{16}H_{10}$

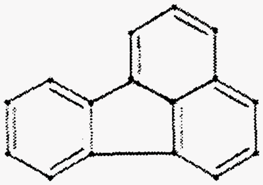
(202)



$C_{16}H_{10}$

(202)

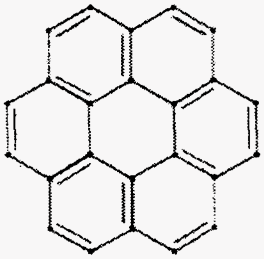
FLUORANTHENE



$C_{14}H_{10}$

(178)

CORONENE



$C_{24}H_{12}$

(300)

FOOTNOTE
1. Elementary Hydrocarbon Formula
2. Nominal Molecular Weight

FIGURE 4
General Physical Structure of
Dioxin-Like Compounds

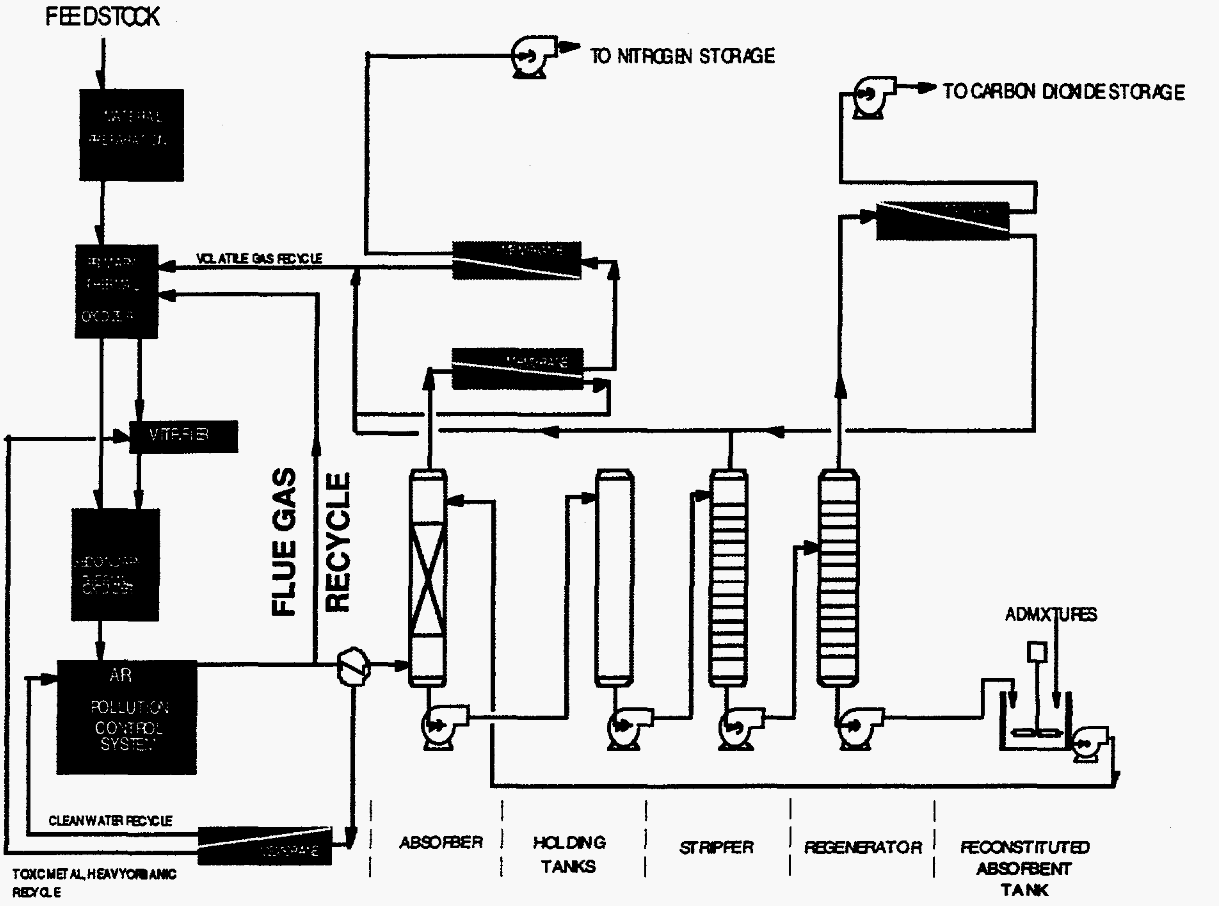


FIGURE 5
Extended Toxic Emission Control System

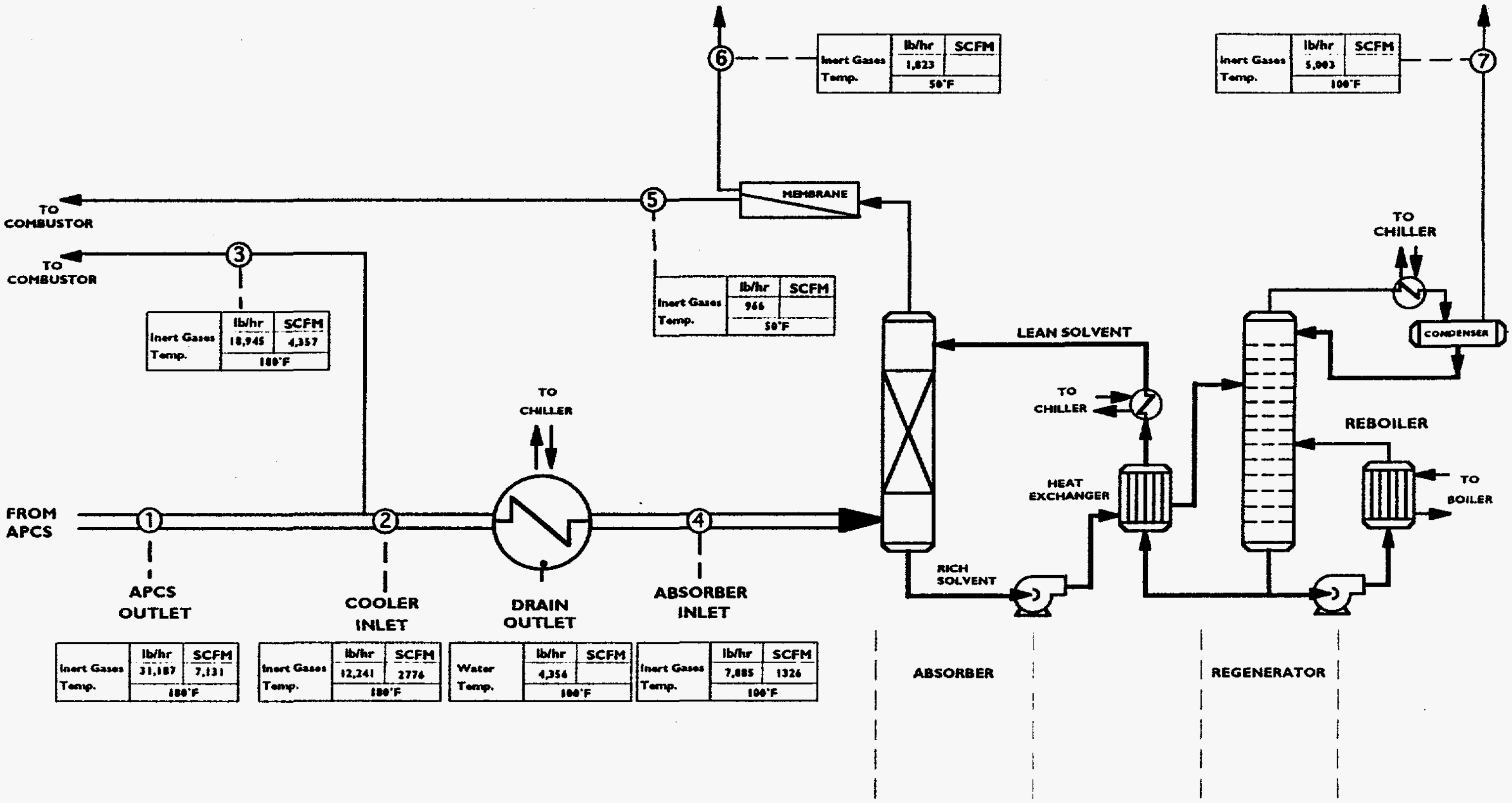


FIGURE 6
Simplified Chemical Absorption Flow Schematic
with Inert Gas Mass Balance

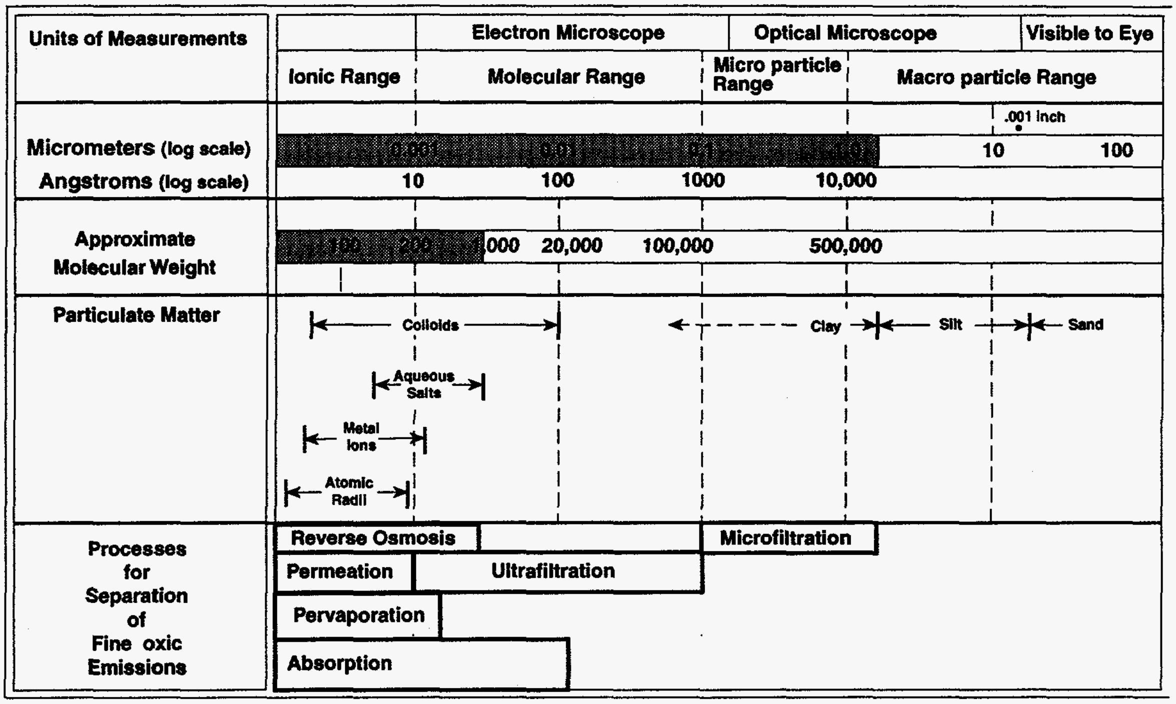


FIGURE 7
Particle Size versus
Filtration Spectrum and Membrane Separation Ranges

FIGURE 8A
Single Stage/Single Cylinder Configuration

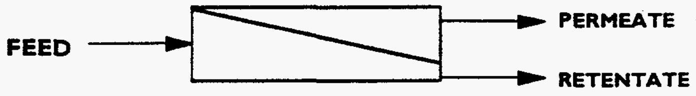


FIGURE 8B
Two Stage/Single Cylinder Configuration

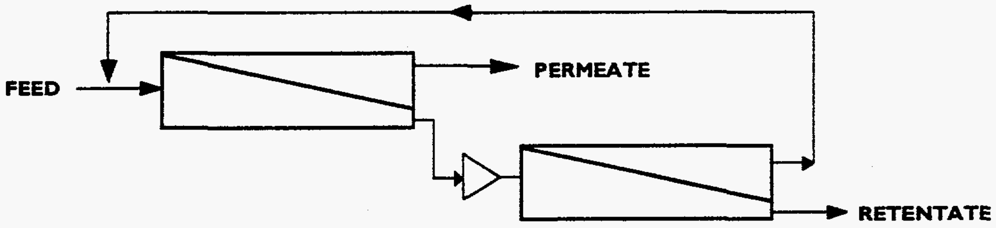


FIGURE 8C
Two Stage/Multiple Cylinder Configuration