J. ENVIRON. SCI. HEALTH, A31(7), 1801-1825 (1996)

Removal of Carbon Dioxide in Closed Loop Off-Gas Treatment Systems

M.K. Clemens P.A. Nelson W.M. Swift
Chemical Technology Division
Argonne National Laboratory
9700 South Cass Avenue
Argonne, IL 60439

Abstract

A combustor with a closed loop off-gas recirculation system has been constructed to demonstrate a gas treatment and purification system that can be installed on hazardous and mixed-waste incineration and vitrification equipment to virtually eliminate the potential for release of hazardous or radioactive materials to the environment. In initial tests, a 250,000 BTU/h (75 kW thermal) combustor was operated in an open loop to demonstrate the removal of combustion product CO_2 in a fluidized bed of CaO (lime), and particulates were removed with hot gas candle filters. An absorbent solution treatment (AST) process is now being developed for removal of CO_2 from a side loop. High CO_2 concentrations can be maintained in the recirculating gases, and this improves the performance of commercially available processes used to purify gases and produce CO_2. Incineration systems with closed loop off-gas treatment can have a high throughput and accommodate more hazardous and more radioactive waste streams than what would be possible with a conventional incinerator. With the AST process, CO_2 and water vapor go through two changes of state before release, effectively separating these combustion products from contaminants released during incineration or vitrification. Oxygen is added to support combustion, and solids are separated by precipitation and filtration.

Introduction

Overview

This paper discusses how commercially marketed technologies for removal and recovery of CO_2 can be adapted for use on closed-loop incineration systems. This paper also describes an Argonne National Laboratory (ANL) concept, the absorbent solution treatment (AST) process, which is based on modifications to commercially demonstrated gas purification technologies. In this process, a side-loop system is added to the main loop for removing CO_2 in scrubbing towers using aqueous-based CO_2 absorbents. The remaining gas is returned to the incinerator with oxygen addition. The absorbent solution is regenerated by driving off the CO_2 and water vapor, which are released to the atmosphere. Contaminants are either recycled for further treatment or form precipitates which are removed during the purification and regeneration process. There are no direct releases of gases or particulates to the environment. The CO_2 and water vapor go through two changes of state before release, effectively separating these combustion products from contaminants released during incineration.

Due to the fact that the AST process can accept a wide range of wastes, the need for frequent sampling and characterization of the feed material and treated waste streams is minimized. Off-gas treatment equipment can be cost effectively optimized and not over designed to handle upset conditions. Contaminants can be captured at several points in the AST process and removed or recycled for additional treatment. The system may be retrofitted to existing facilities or included in the designs for new installations.

Background

Hazardous and mixed wastes containing organic materials have built up at many DOE and DOD sites over a period of decades. One option is to construct and operate centralized incineration facilities and ship the wastes to these facilities for disposal. The many different types of waste would require extensive sorting, separation, and characterization of materials. Campaigns lasting several days or weeks would have to be carried out so that a uniform feed stream could be fed to the incinerator.

A flowsheet for off-gas treatment in typical mixed-waste incineration is shown in Figure 1. The gas from the incinerator is partially quenched to about 150 °C to precipitate volatile metals, which are removed with the fly ash in a

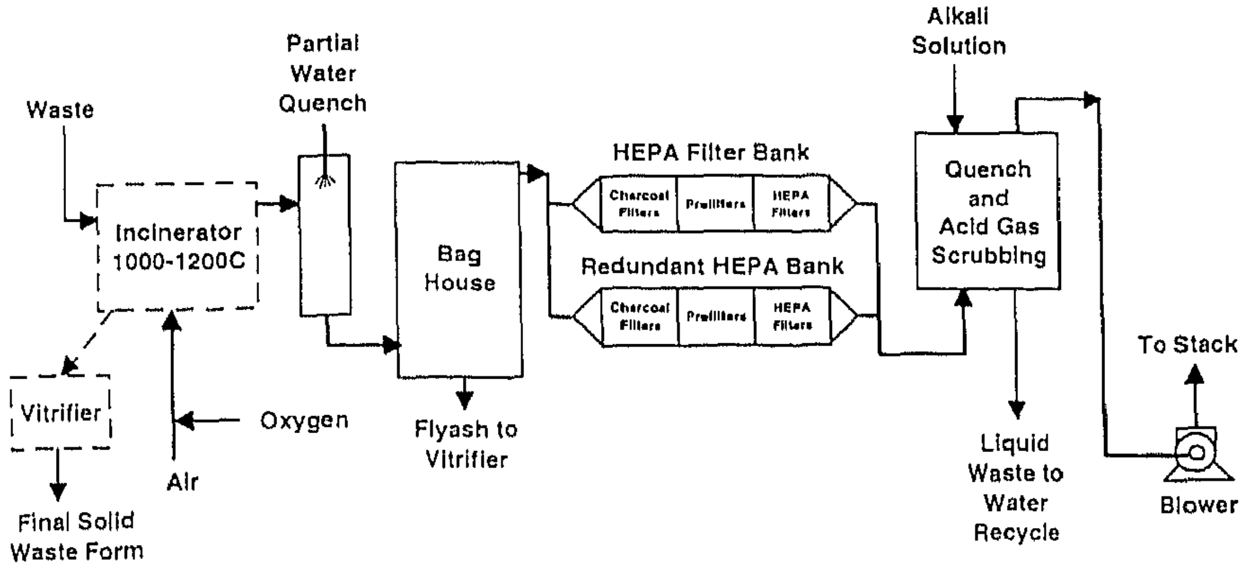

Figure 1: Typical system for off-gas treatment for mixed-waste incineration.

baghouse following the partial water quench. The particulate matter from the baghouse is essentially free of chlorides and is, therefore, suitable for mixing with the incinerator bottom ash for treatment in a vitrifier. The off-gas from the baghouse is then passed through filter banks containing charcoal filters to remove mercury and high efficiency particulate (HEPA) filters to remove fine particulate matter, especially radioactive materials. The off-gas is then scrubbed in packed towers to reduce the chloride and sulfur concentrations to low levels and is released to the atmosphere through a stack or chimney.

This type of off-gas treatment provides a direct flow path from the incinerator to the stack outlet release. Operators of incinerators have had a difficult time convincing the regulatory and public stakeholders that there will be no transient or upset conditions which could lead to an unacceptable release of hazardous materials.

Need for Closed Loop Off-Gas Treatment

Off-gas treatment systems perform best when the incinerator variables such as feed material composition, feed rate, temperature, off-gas volume, and residence time are maintained in a steady-state condition. Existing off-gas treatment systems rely on proper operation of equipment, including controls and monitoring instrumentation, to prevent accidental releases of hazardous materials from the stack. Currently available equipment cannot instantaneously detect and prevent these releases in open-release systems. Unacceptable releases may occur during a transient condition or in a subsequent shutdown and restart process. Existing off-gas treatment equipment must be sized to handle the large gas volumes associated with worst-case operating conditions and include spare or redundant features. This conservatism has a cost impact and can detract from system performance during normal operation.

Argonne set out to develop a closed loop off-gas treatment system that could accommodate start-up, shutdown, and other transients while eliminating the potential for uncontrolled releases of hazardous materials to the environment. Argonne's first attempts to develop a delayed release or unvented incineration process for hazardous and mixed wastes were based on the use of a fluidized bed of lime (CaO) operated at about 600 °C to absorb CO_2. In preliminary tests, open-loop flow experiments were carried out to determine the rate of absorption of CO_2 in the lime bed. The experiments were successful in that the feasibility of absorbing CO_2 by this method was demonstrated. More recently, however, we have concluded that the use of an aqueous absorbent solution is more cost effective on larger off-gas systems, has operational advantages, and produces a minimum of wastes requiring final disposal. Aqueous absorbents can be easily stored and pumped through the absorption, purification, monitoring, and regeneration processes and then recycled.

Energy and material balances for closed-loop systems must include iterative calculation techniques to identify the steady state compositions of all process streams. Argonne National Laboratory developed a calculation technique which uses the Microsoft EXCEL spreadsheet for personal computers. The input data for the program includes material feeds, combustion reactions, heat capacities, and heats of formation of all material streams. The calculations are based on recycle of main loop gases and absorption of CO_2 in a side loop. Inert gases, primarily nitrogen, that enter the system are included in the material and energy balances. The effect of system parameter changes can be evaluated and presented in spreadsheet format after less than one minute of computing time on a Pentium PC. This program showed that a high CO_2 concentration can be maintained in the closed loop by providing a side loop for removal of CO_2 and removing water vapor, sulfur dioxide, and chlorine by devices in the main loop.

This paper first describes the work performed at ANL to develop an unvented process that uses a fluidized bed of lime to remove CO_2. A review is then made of commercially developed technologies that are being marketed for removal of CO_2 from off-gas streams. Finally, the approach selected by ANL for CO_2 removal from a side stream with an inorganic aqueous absorbent solution is described.

Unvented Thermal Process

Mixed wastes at ANL are currently packaged and shipped off-site to DOE mixed-waste storage facilities such as the Hanford Site Central Waste Complex. The largest volume of mixed waste accumulated at ANL is scintillating counting fluid waste. Vials of this toluene-based fluid are stored in 55-gal drums and cushioned with a vermiculite absorbent. Biological wastes, solvents, and lubricating oils used in radioactive areas can also be classified as mixed wastes and require off-site disposal. The future availability of this storage option for ANL-generated wastes cannot be assured. The nuclear power and medical industries are also feeling the impact of disappearing options for disposal. Installation of a conventional hazardous-waste incinerator at ANL is not an option.

At ANL, we identified the need for a closed-loop incineration system that produced no direct releases to the environment. Our initial concept was based on recirculation of combustion gases. Combustion-product water vapor was removed in a condenser, carbon dioxide was absorbed in a fluidized bed of lime (CaO), and oxygen was added in the recycle loop to support combustion.

The recirculating gas used for fluidization contains nitrogen, which enters the system as an impurity in the oxygen feed and during the destruction of some organic compounds such as amines. A small amount of this nitrogen must be separated to a side stream for purification and release. Welded construction is used to minimize in-leakage of atmospheric gases to the combustor and recirculation system. This closed-loop process for thermal and chemical remediation of mixed waste was patented [1] and discussed in a paper presented at the 1993 International Incineration Conference [2].

The CO_2 absorption unit in this process is a fluidized-bed reactor containing a bed of calcined limestone (CaO), which reacts with acid gases given off during oxidation of organic materials. Gases that will react with CaO include CO_2, SO_2, HF, HCl, and HBr.

The most flexible arrangement for the equipment involves separating the processor into two separate units: an oxidizer and a carbon dioxide sorber, as shown in Figure 2. The oxidizer can be operated at high temperatures (700–900 °C) to ensure complete oxidation, whereas the sorber can be operated at a lower temperature (500 °C) appropriate for CO_2 sorption. In this process, the oxidizer could be

- a fluidized bed with a mixture of sand and lime for bed material;
- a slagging combustor;
- an electrically heated vitrifier; or
- various conventional incinerators.

In all cases, the gas from the sorber is cooled to condense the water and recirculated to the oxidizer with sufficient oxygen to support combustion. Lime is continuously fed to the sorber bed and continuously withdrawn through an overflow pipe or bed drain. The pressure in the system will be controlled at slightly less than atmospheric pressure to assure that any leaks in the system do not result in the escape of hazardous materials.

If all of the reaction products are converted to cement, the total volume of the waste material might be somewhat larger than the initial organic waste volume because of the conversion of carbon in the organic material to $CaCO_3$. This might be acceptable for small producers of hazardous or mixed waste, because a moderate increase in a small volume of waste is not important, and more serious problems than the waste volume are solved by the new processing scheme. The process should also be considered for treatment of off-gases from electrode or plasma-torch-heated vitrifiers due to their relatively small amount of off-gas production. For low organic content waste feeds, it may be possible to eliminate the secondary combustor because unburned organics are either recycled or destroyed in the absorption and calcination process.

A thermal regeneration step may be added to the above processing scheme to reduce the amount of solid wastes and to generate fresh lime for the absorption process, as shown in Figure 3. Spent lime (mainly calcium carbonate) would be calcined in a separate unit to decompose the $CaCO_3$, recover the lime, and release CO_2. The most energy efficient form of this process would be to transfer the hot bed material from the sorber to the calciner without cooling. To facilitate the reuse of the spent lime leaving the sorber, it would be advantageous to add lime to the oxidizer if acid gases such as SO_2, HF, HCl, or HBr are being produced. This will retain sulfur and the halogens in the oxidizer ash. The source of the lime for the oxidizer would be

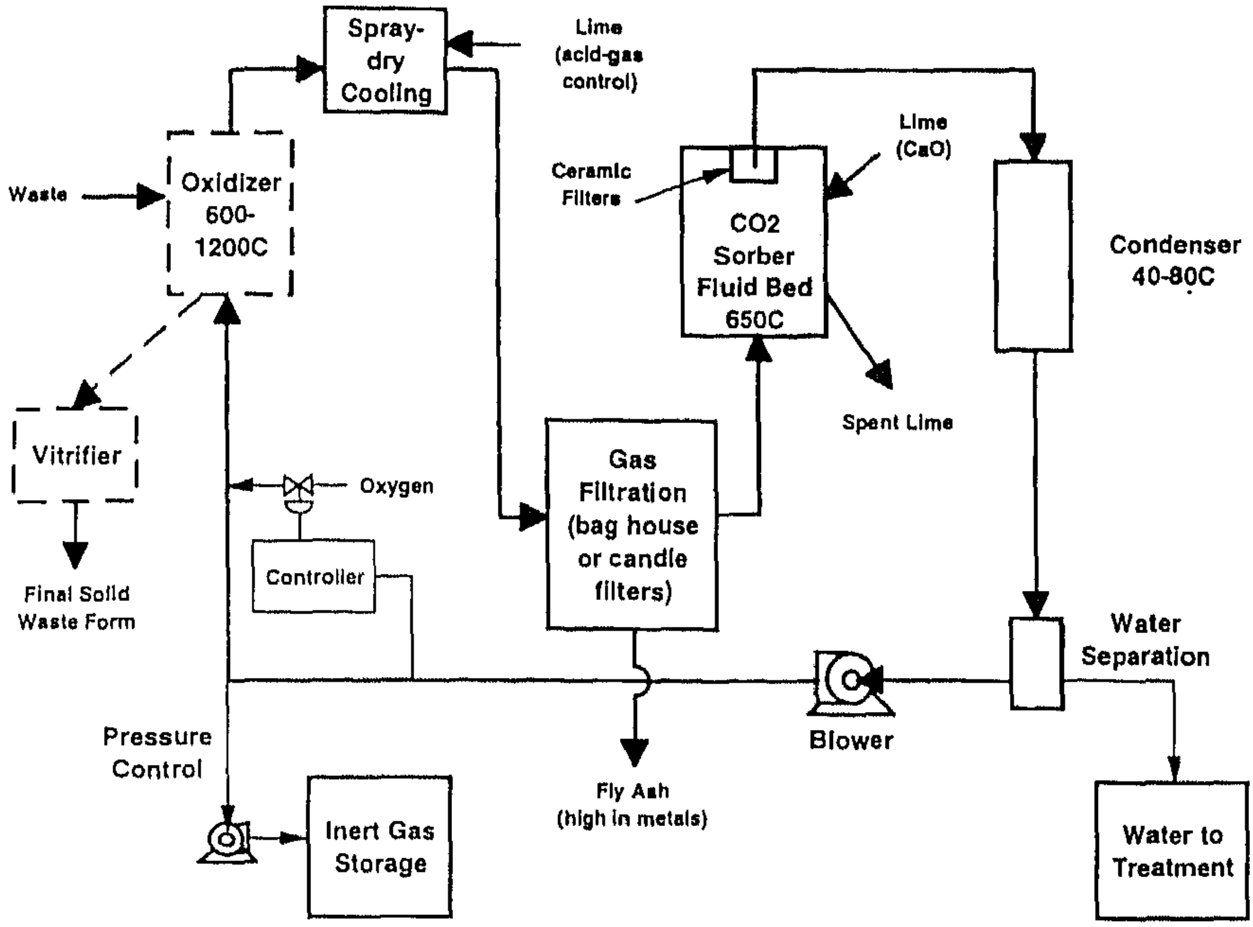

Figure 2: Gas handling system for unvented mixed-waste treatment.

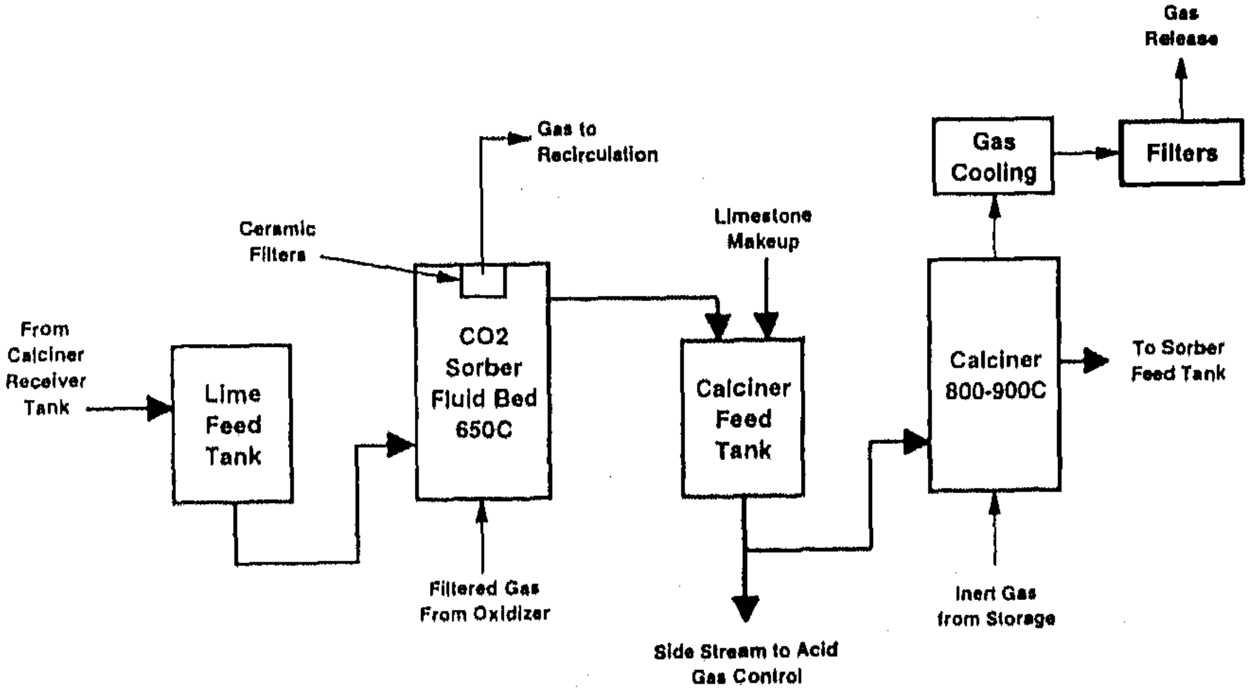

Figure 3: Lime recovery system.

a small side stream taken from the spent lime in the sorber. Thus, the only solid waste stream from the process would be the ash from the oxidizer. The volume of ash per unit mass of waste destroyed would be about the same as for a standard fluidized-bed incinerator to which limestone is added to retain the acid-gas anions with the ash.

The destruction of the organic material, absorption of CO_2, and decomposition of the $CaCO_3$ are carried out in separate steps in different equipment. This method greatly reduces the potential for the release of toxic materials compared with that associated with standard incinerators. Only gases enter the sorber, and these are almost entirely free of the hazardous organics fed to the oxidizer. Most of the gas, including unreacted organics, will pass through the sorber and be recirculated to the oxidizer. To minimize the amount of organic material released from the calciner, it must be indirectly heated and thus involve no air or sweep gas addition. Under these conditions of restricted gas addition, no gas is released from the calciner if the temperature inadvertently drops below the minimum calcining temperatures of 800–900 °C . This approach results in long retention times at high temperatures for destroying the tiny fraction of organic gases that may be clinging to the spent lime. The off-gas from the calciner as operated above would be more than 99% carbon dioxide with small amounts of oxygen and nitrogen. Its volume per unit of waste destroyed would be about 10% of that from a conventional incinerator. The off-gas treatment system required for this carbon dioxide stream would consist of cooling and filtering equipment, and should be relatively inexpensive.

If the waste to be treated contains hazardous metals or radioactive solids, it may be appropriate to vitrify the ash from the oxidizer. Alternatively, the oxidizer may be operated at an enriched oxygen level to produce a glassy slag directly.

Experimental

The closed-loop process is being developed and tested at a pilot-scale fluidized-bed combustion test facility located in the Chemical Technology Division at ANL. The combustor has been converted from a fluidized-bed, coal-burning facility to a test unit for closed-loop off-gas treatment. The conversion involved addition of a gas recirculation system, including hot-gas candle filters, a condenser, a water collection tank, connections for installing CO_2 absorption equipment, a pump and collection tank for drawing off a small stream to avoid inert gas buildup, and a gas recirculation pump. Figure 4

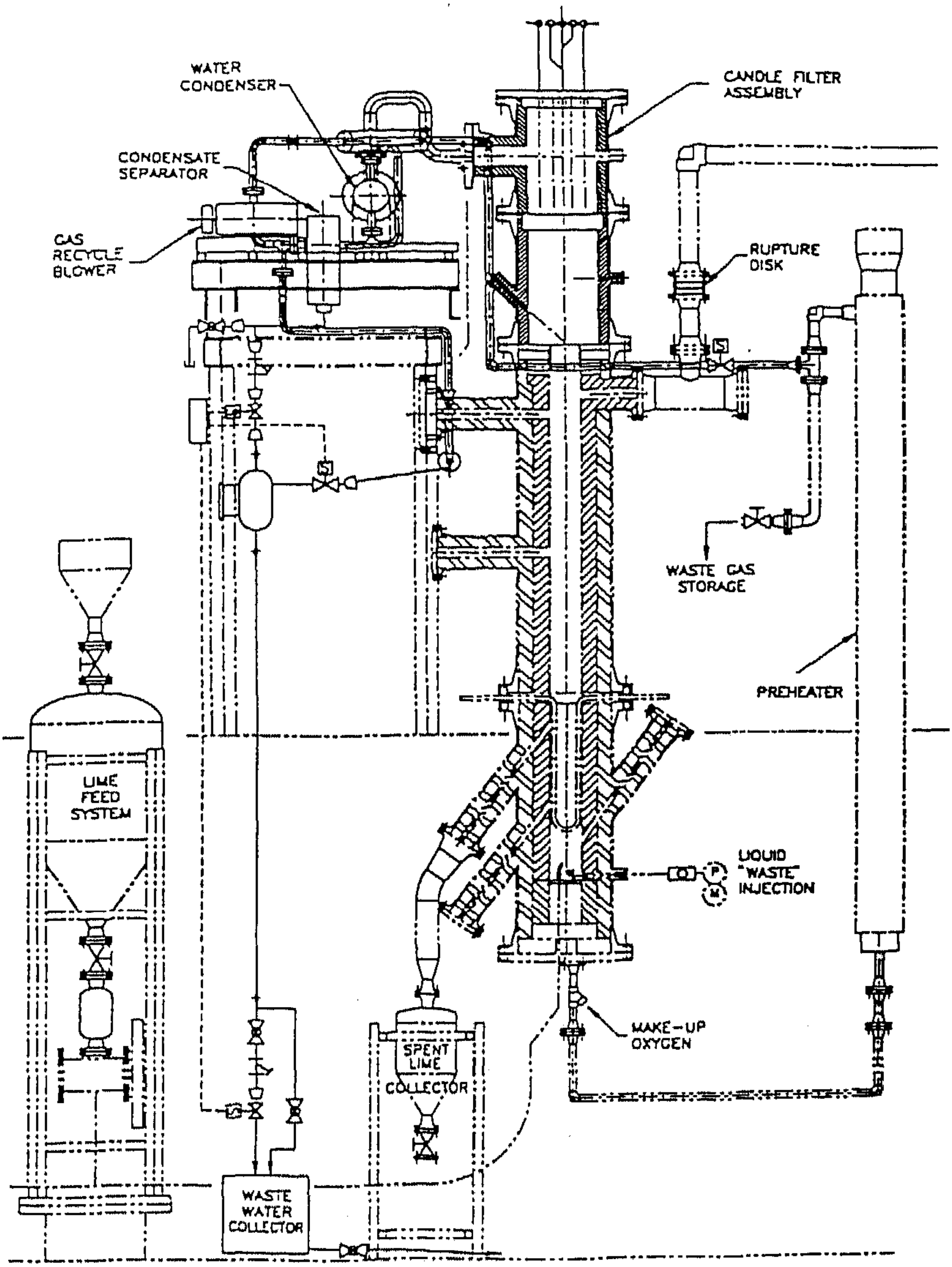

Figure 4: Experimental fluidized-bed processor designed for gas recirculation.

shows the closed-loop configuration of the experimental fluidized-bed processor as modified for gas recirculation.

The fluidized-bed combustor has a 15-cm diameter distributor plate. It is cooled by boiler tubes and has a capacity of approximately 250,000 Btu/h (75 kW) at 1 bar (100 kPa) pressure and 70% oxygen. The combustor and hot gas filter system are enclosed by 46-cm diameter pressure vessels. All components, piping, and instrumentation can be operated from the main floor and from two existing mezzanine level floors. An overhead traveling bridge crane is used for installation and maintenance.

Preliminary tests were performed with the fluidized-bed combustor prior to its conversion to a closed-loop system. Toluene was combusted in once-through flow experiments to determine the rate of absorption of CO_2 in the lime bed. The combustion chemical process is:

$$C_7H_8 + 9O_2 + 7CaO \longrightarrow 7CaCO_3 + 4H_2O \tag{1}$$

Typical results from the initial once-though tests are presented in Figures 5 and 6. Figure 5 compares the measured CO_2 concentration in the gas leaving the fluidized bed of lime with the calculated equilibrium concentration (at the bed temperature) and the calculated CO_2 concentration assuming 0% removal by the lime. Initially the measured CO_2 concentration exceeded the calculated value due to the calcination of a small amount of $CaCO_3$ in the lime bed. Once the bed temperature was low enough, the measured CO_2 fell between the lower equilibrium limit and the upper calculated limit. Indirectly evident in Figure 5 from the increasing calculated CO_2 value is the fact that as the test progressed, the toluene feed rate to the fluidized-bed combustor gradually increased to try to maintain the bed temperature at 650 °C. Toluene has a high auto-ignition temperature, and effective combustion at the planned test temperature could not be maintained.

Figure 6 illustrates the extent of CO_2 removal and the degree of lime utilization that were calculated from the data in Figure 5. As the bed temperature gradually declined during the test, both the CO_2 removal and the lime utilization increased, as expected. The results are from preliminary tests and do not necessarily represent what could be achieved under optimized conditions. The initial tests were successful in that they verified the need for a high temperature oxidizer separate from a low temperature lime absorber operated at approximately 500 °C. We also learned during these initial tests that the ANL fluidized-bed combustor could be operated at relatively low com-

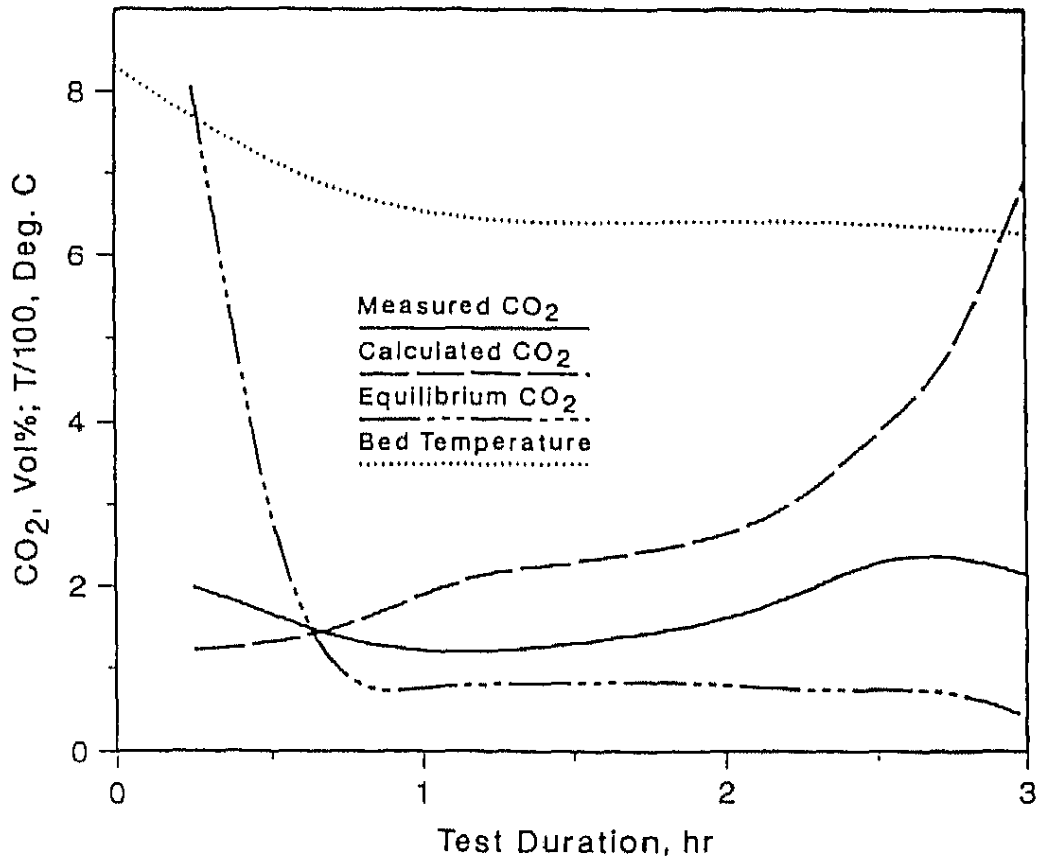

Figure 5: Once-through tests - temperature and CO_2 data.

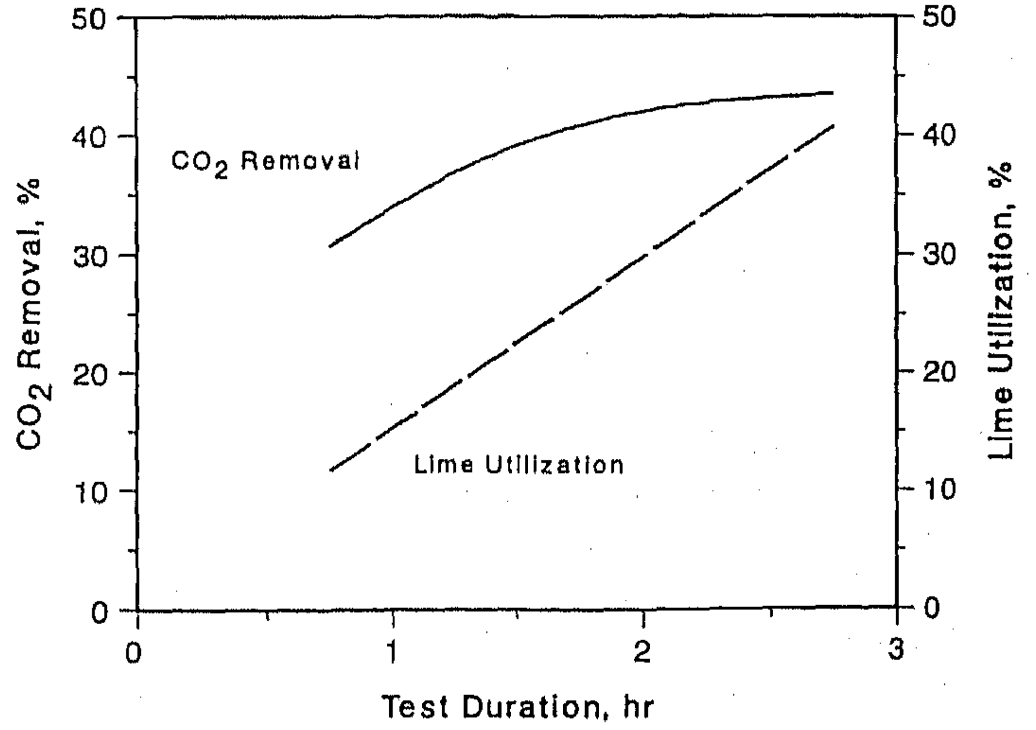

Figure 6: Once-through tests - CO_2 removal and lime utilization.

bustion temperatures to produce an off-gas stream high in untreated organics that could be used to test operation of off-gas treatment systems.

We believe that the lime-based process with the separate absorber operating at optimum temperature would be a good selection for small waste streams where a concrete product is desirable, where an indirectly heated calciner can be used to regenerate the sorbent, and where the spent absorbent can be monitored for purity and then calcined in a commercial cement-making facility in which any residual organic contaminants are destroyed [3].

The following experimental work is needed to provide data necessary for scale-up of the fluidized bed of lime process and to support technology commercialization:

1. Operation of the currently installed pilot-plant scale closed-loop combustion and off-gas treatment system on a waste stream that has a low auto ignition temperature. This will allow for effective in-situ absorption of CO_2 in a single oxidation/absorption vessel.
2. Addition of a separate combustor so that the waste can be oxidized at high temperature, and the CO_2 absorbed in the existing fluidized bed at optimum temperature.
3. Pilot-scale or bench-scale demonstration of an indirectly heated calciner to regenerate the absorbent for re-use. The fate of impurities and hazardous materials needs to be determined.

We have now directed our efforts toward development of a closed-loop off-gas treatment system which uses an aqueous absorbent solution for CO_2 removal. The system includes modules or stages which can be optimized to treat off-gas streams from various thermal treatment processes.

Carbon Dioxide Recovery from Combustion Flue Gas

Electric-generating station boilers and industrial furnaces that burn fossil fuels such as coal, oil, and natural gas are sources of flue gas for the commercial production of CO_2. The concentration of CO_2 in a flue gas stream is dependent on the quantity of carbon in the fuel and the combustion stoichiometry. Current uses for CO_2 include pure CO_2 product, feedstock to manufacture chemicals such as soda ash or urea, alternative feedstock for chemicals containing carbon and oxygen, freezing or chilling of food, carbonation of beverages, solvent for supercritical extraction, replacement for chlorinated fluorocarbons, replacement for stronger acids for pH control in water-based industries, and for tertiary oil recovery [4].The U.S. CO_2 market is expanding on the order of 5% per year and the average selling prices range from \$50 to \$70 per ton [5].

The quality specification is 99.98 wt % minimum for food grade CO_2 and 99.97 wt % minimum on a dry basis for chemical grade product [6]. These specifications and the limits for impurities (sulfur compounds, nitrous oxides, and hydrocarbons) are exceeded by absorbent solution processes in current use. Concerns over global warming are leading to continued interest in processes which remove CO_2 from combustion gases and recover it for use in industrial processes.

A patent was first granted in the 1930s for use of alkanolamine solutions as absorbents for acid gases. Monoethanolamine (MEA) is the alkanolamine solution typically used in commercial facilities which recover CO_2 from flue gas. Skid-mounted units have been installed to recover CO_2 for use in the food and beverage industries [7]. Pilot-plant testing at a Canadian pulverized-coal burning facility was performed to evaluate two patented amine-based processes [8].

Alkanolamine solutions remove CO_2 from flue gas because they chemically react with CO_2, which dissolves in the water to form an acid and then reacts with the basic organic material in solution. As the solvent is regenerated, chemical absorption occurs at flue gas pressure with CO_2 desorption by heat at near atmospheric pressure.

The first patents for absorption of CO_2 in a hot solution of potassium carbonate were issued in Germany in the early 1900s. The hot potassium carbonate process was further developed by the U.S. Bureau of Mines as part of a program to derive liquid fuel from coal. Benson and Field conducted much of this work and patented improvements in the 1950s. Their developments produced the "Benfield process," which has been licensed to industry with continuing process and corrosion inhibitor improvements [9]. Industrial activities which use one variation or another of this technology include production of ammonia, purification of hydrogen for refinery use, purification of natural gas to pipeline quality or prior to cryogenic liquefaction, production of ethylene oxide, production of vinyl acetate, and purification of coal-derived synthesis gases [10].

The conventional alkanolamine and alkaline salt systems use basic solutions with either an organic hydroxyl amine or an inorganic base, such as potassium carbonate (K_2CO_3), for CO_2 absorption. The CO_2 is removed from the flue gas at 0–100 psig (0–690 kPa) in an absorber column, which operates at 40–85 °C. The regenerator column typically operates at 100–130 °C and 2–20 psig (14–140 kPa). Because the solvent contains water, steam is generated from the solvent by a reboiler rather than by direct injection of steam to avoid either concentrating or diluting the solvent. Pressure reduction or vacuum operation at constant temperature can also regenerate the absorbent solution.

The recovery of CO_2 from flue gas is complicated by the composition of the flue gas and by the low partial pressure of CO_2, both of which are a function of the combustion fuel composition. Impurities in the flue gas which can significantly affect the CO_2 removal system design include oxygen, acid components such as NO_x and SO_x, and fly ash or other particulates.

Because conventional alkanolamine and alkaline salt systems rely on acid-base reactions to absorb CO_2, any acids present in the gas that are stronger than CO_2 will be absorbed preferentially to CO_2. Such stronger acids include NO_x and SO_x, both of which react irreversibly with the amine or K_2CO_3 and cause it to degrade into compounds or form salts that are inert to CO_2 and are more corrosive than the solvent. Also, any oxygen present in the feed gas irreversibly reacts with and degrades amines such as MEA, and hazardous waste sludges are produced which must be removed [11]. The CO_2 absorbed in the solvent and salts and the solvent degradation products tend to corrode aqueous solvent systems in this service. To minimize corrosion, either constant solution purification is required, or corrosion inhibitors must be used. Suppliers of commercial CO_2 removal systems use proprietary corrosion inhibitors to minimize system corrosion and activators to improve solution effectiveness [4].

One concern about the use of alkanolamine-based solutions is hydrocarbon solubility. The more chemically alike are a solvent and a solute, the greater their solubility in one another. The less aqueous a solution is made by increasing its amine content, the greater will become its affinity and solubility for hydrocarbons [11].

Benfield solutions contain 20–35% potassium carbonate (K_2CO_3) with small quantities of a corrosion inhibitor and an activator that catalyzes the rates of absorption and desorption. Two types of activators are in use: an organic activator for nonoxidizing environments and an inorganic activator for oxidizing environments. For flue gas, the inorganic activator is used [12]. The Benfield-process inorganic solvent is a weaker base than the organic solvent system, and the rate and heat of absorption are lower for the inorganic solution of potassium carbonate. The Benfield-process equipment is larger than that required for the organic solvent. This disadvantage is offset by the fact that off-gas entering the Benfield process can be at a higher temperature and have less pretreatment. The Benfield process requires significantly lower regeneration heat requirements [4].

Off-gases from incineration processes include excess oxygen and NO_x, and may contain hazardous organic material. The hot potassium carbonate (Benfield) process is better able to handle these problem gases than the amine-based systems because hydrogen, nitrogen, and hydrocarbons are essentially insoluble in the potassium carbonate solution. The Benfield process has been effectively used on oxygen- and NO_x-bearing streams, such as blast-furnace gas and ethylene-reactor recycled gas [4].

Mixed wastes such as spent cationic-exchange resins burn rapidly due to their high heat content. They contain approximately 30% sulfur, and their incineration overloads acid-gas scrubbing equipment [13]. This overload would be captured in the Benfield solution and be removed by filtration of the non-soluble K_2SO_4 salt. Nitrogen dioxide in the off-gas would be partially absorbed and would form potassium nitrate (KNO_3), a non-regenerable salt. Nitric oxide has a low solubility in the aqueous solution [4]. Products of incomplete combustion and other organics remain in the gas stream and are returned to the combustor or incinerator for additional treatment.

The concentration of KNO_3 in the circulating solution is controlled by cooling a side stream and treating it for precipitation of KNO_3. The solubility of KNO_3 in the Benfield solution is a function of temperature and K_2CO_3 concentration; lowering the temperature and increasing K_2CO_3 concentration causes KNO_3 to precipitate. Potassium ion makeup, required due to its loss with nitrates, is added to this side stream as K_2CO_3. This step increases the K_2CO_3 concentration and helps to precipitate KNO_3. The amount of NO_x in the CO_2 product is negligible [12].

The CO_2 product from the Benfield unit is more than 99.9% pure on a dry basis. The solubilities of nitrogen and oxygen from the flue gas are very small in the aqueous solution, especially at low pressure. Other impurities such as NO_x are also low, typically less than 1 ppm [12]. Halides form soluble potassium salts that build up in the system until they are removed by precipitation or crystallization.

Absorbent Solution Treatment

The absorbent initially selected for the AST process developed at ANL is an inorganic aqueous solution of potassium carbonate, which forms potassium bicarbonate when reacting with CO_2 and water. Organic absorbent solutions such as monoethanolamine can also be used with the AST process.

The inorganic potassium carbonate absorbent is preferred due to the relative insolubility of hydrocarbons, the relative ease in detecting and removing contaminants, and its performance being unaffected by oxygen in the feed gas. Hydrocarbons tend to be soluble in the organic solution of MEA, and the presence of hazardous organic material would be difficult to detect. Oxygen in the off-gas degrades organic solutions and forms additional hazardous materials which must be removed. These degradation products could be identified as a newly formed mixed waste if radioactive materials are being treated. The existing ANL patent for "Thermal and Chemical Remediation of Mixed Waste" is being extended to include the AST process. A flowsheet for the AST process is shown in Figure 7.

The combustor and closed loop recirculation system are operated at less than atmospheric pressure so that any leakage will be into the system. Particulates are removed from the recirculating stream by a conventional baghouse. The gas that would normally be released up the stack is cooled in a condenser to remove the moisture added in the water quenching steps. The main stream of cool, relatively dry gas is returned to the incinerator with an oxygen addition. Because the gas is not released, HEPA filters are not used for the recirculating gas but may be needed for the relatively small stream that is released later in the process. Carbon dioxide and additional water vapor are removed in a side stream. The use of a side stream, rather than absorption from the main stream, raises the CO_2 concentration at the inlet of the CO_2 absorber and, therefore, reduces absorber size, installation cost, and operating cost. The Benfield process can be effectively used at atmospheric or subatmospheric pressure due to the high CO_2 concentration in the closed-loop process. The recirculating loop and CO_2-removal side-loop equipment can be constructed of pressure vessels interconnected by piping systems which use all welded valves and components. This would allow operation of the gas absorption process at an elevated pressure to further reduce equipment and operating costs.

Absorbed contaminants build up in the absorbent solution and are separated during the purification process by precipitation and crystallization. These solids are then removed by filtration of the liquid absorbent. The liquid absorbent from the filter is purified from any organic carbon transferred from the off-gas by means of a partial gas release stage. The CO_2 and water vapor given off in this stage, strip organic materials of low solubility from the solution. The gas thus given off is combined with the off-gas from the CO_2 absorber, and the combined gas is returned to the main loop, which returns gas to the incinerator. The purified CO_2 absorbent would be continuously

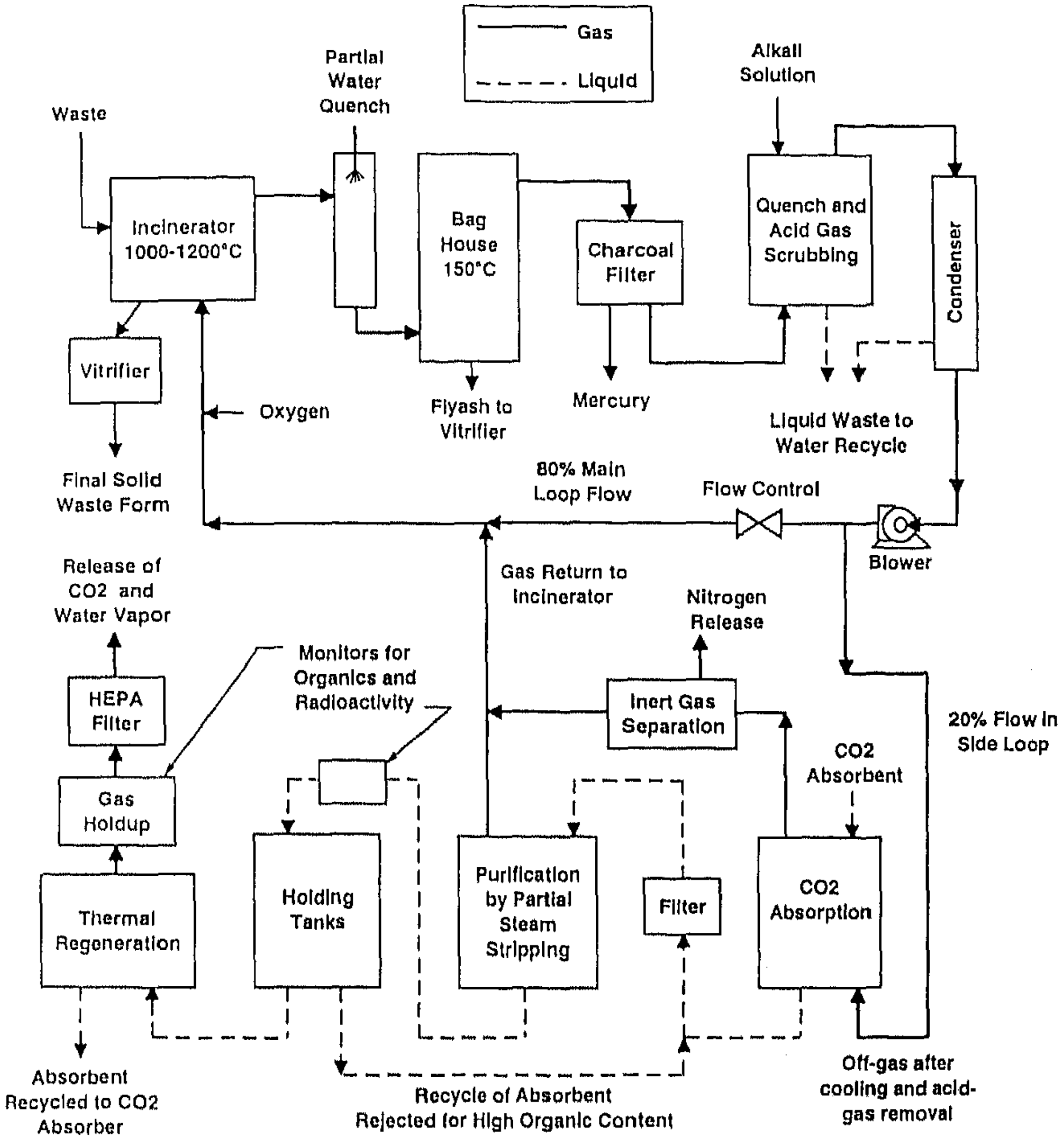

Figure 7: Absorbent solution treatment of gases from mixed-waste incinerators.

monitored for organic carbon as it leaves the purification system and enters holding tanks. For hazardous waste incineration, these tanks would each have a 10-min retention capacity and would alternate in filling, holding, and then dumping their contents to a feed tank that would feed the gas release stage. Liquid absorbent that did not pass the analytical test for organic carbon would be recycled through the purification system. In the gas release stage, the reaction products (CO_2 and water) which are generated in the incinerator would be released by raising the temperature or lowering the pressure. The regenerated absorbent would be recycled to the CO_2 absorber. There are no direct paths for gases produced during incineration to enter the environment (CO_2 and water vapor released from the process undergo two changes of state after entering the side loop).

For mixed-waste incineration, the off-gas from the regeneration of the purified absorbent solution must have a final monitoring count for α, β, and γ activity prior to its release through a HEPA filter. A 30-min holdup time may be required to detect any low levels of radioactivity in the off-gas stream.

Inert gases, primarily nitrogen, will tend to accumulate in the closed-loop process and must be removed to maintain a slight subatmospheric pressure in the combustor recirculation loop. The nitrogen is introduced as a 0.5% impurity in the oxygen supply, from the combustion of nitrogen-containing materials and in-leakage to the system. This small stream of inert gases can be removed by membrane separation, monitored, and released. Inert gases from the AST process should not be difficult to separate because the particulate and acid gases have been removed during preliminary off-gas treatment steps. Stull et al. reported on gas separation membranes which could be used to treat off-gases from thermal incineration processes. However, additional development work needs to be done to identify reliable membranes that can be directly used on untreated incineration off-gas streams [14].

Not only does the closed-loop process provide many additional mechanisms for removal of toxic material, this process also provides (1) a mechanism for monitoring the absorbent from which both CO_2 and water are released to the stack prior to the release, and (2) a means of recycling and purifying materials that do not meet specification. With the closed-loop system, it will be possible to safely treat the type of high-level mixed wastes and transuranic wastes that are currently being sent to storage facilities. Department of Defense wastes generated during facility remediation and toxic chemicals such as pesticides and PCBs could also be treated safely in closed-loop systems.

Figure 8 is a simplified flow diagram of the fluidized-bed test oxidizer, ceramic candle filters, and closed-loop gas treatment equipment currently installed at ANL. Figure 8 also shows the planned addition of a combination absorption and regeneration test unit to remove CO_2 from a side loop. The system will include the pumps, controls, and solution tanks that are necessary for system operation.

Work is needed to determine the extent to which volatile contaminants such as iodine, technetium, mercury, and fine particulates enter the absorbent solution. Separation methods for removal of soluble and insoluble contaminants need to be evaluated, and the need for new processes identified. A Fourier transform infrared (FTIR) spectrometer system developed at ANL will also be evaluated for use in monitoring the presence of contaminants in the process [15]. The FTIR has a response time of 6 min and can identify almost all organic compounds and atmospheric gases such as SO_2, NO_x, CO, CO_2, NH_3, HCl, and O_3. Detection of key organic compounds such as methane, benzene, ethylene, and chlorinated hydrocarbons will be evaluated.

As previously noted, removal of CO_2 from a side loop allows for operation of closed-loop incineration systems with a high CO_2 content in the recirculating gases. The side loop CO_2 removal devices are not large because they treat a high CO_2 content side-loop stream. Additional development work may lead to a cost effective hybrid purification process using absorbent solutions and cryogenic liquifaction. Direct removal of CO_2 from the sidestream by liquification should also be considered due to the relatively small volume of sidestream gases and the high CO_2 content.

Combustion with Oxygen

Oxygen is added to closed-loop incineration systems to support combustion of the wastes. Good mixing of fuel and oxygen is needed, and conventional burners may need to be modified or replaced. The use of oxygen normally increases flame temperatures and the tendency for slagging with materials that have low ash-fusion temperatures. The major considerations in the selection of an oxygen burner are the burner's flame temperature and mixing characteristics.

An oxygen burner must rely primarily on high velocity jets to achieve the high momentum needed to produce good mixing. Control of flame temperature may be accomplished by aspirating the furnace gases into the oxidant jets prior to mixing with the fuel. The waste fuel (liquid or gas) is supplied at the burner axis as a relatively low velocity jet. Most of the oxygen is supplied

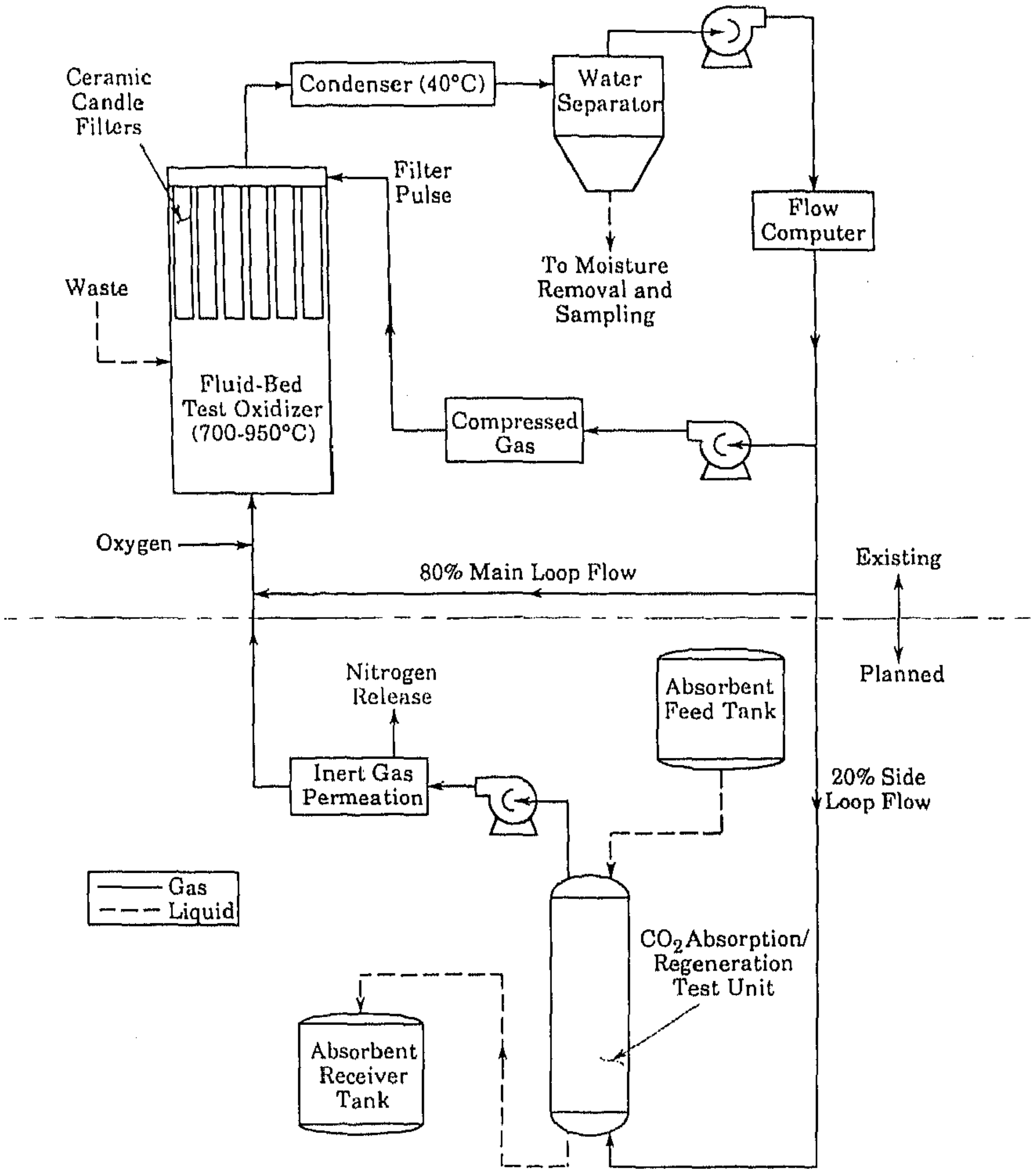

Figure 8: ANL equipment for study of absorbent solution treatment process.

as a ring of high velocity jets surrounding the center fuel stream. The oxygen-rich annulus around the fuel stream enhances flame stability, and the oxygen jets aspirate the fuel and furnace-gas mixture into the burner zone. Enough of the furnace gases are aspirated into the oxygen jets prior to their mixing with the fuel so that the resulting flame temperature is reduced to values substantially below the theoretical flame temperature. M. Ho et al. reported on the demonstration of this Linde-developed burner on the EPA Mobile Incinerator [16]. With this internal gas recirculation design, a portion of the gas must be removed and cooled and then reinjected into the combustor. In other types of combustion systems, oxygen is sequentially added along the path of combustion or added to the recirculated gas to provide a uniform combustion zone temperature.

The use of oxygen in the combustion process instead of air offers significant benefits. The only drawback is the cost of the oxygen. The primary advantage is that the amount of off-gas that must be treated is reduced, and the physical size and capital cost of the off-gas removal and treatment equipment are minimized. Also, thermal treatment capacity is increased, the need for supplementary fuel is decreased, and the generation of thermal NO_x is minimized due to the small amount of nitrogen in the hot combustion zone. The low off-gas velocity in the system maximizes residence time at the high temperatures needed for thermal destruction. Entrainment of small particulate is low. In conventional incinerators, the volatile toxic elements concentrate on the small particulate as the off-gas is cooled. These small particles are carried out of the combustor by the flue gas and are difficult to remove from the off-gas stream.

Equipment Requirements

The closed-loop off-gas system combined with oxygen combustion can be used with almost all types of thermal treatment, incineration, and vitrification equipment. The only restriction is that the equipment should have tight seals so that the thermal treatment portion of the system operates at less than atmospheric pressure. Leakage will be into the system, with no release of untreated materials. Double, rotating seals with a purge gas between the seals should be considered for rotary kiln installations. Depending on the level of radioactivity in the mixed waste, it may be necessary to have a secondary containment shroud around the face of the kiln. This containment would be ventilated to direct any released materials to a filtering device. Plasma arc torches and other types of vitrification equipment produce a large amount

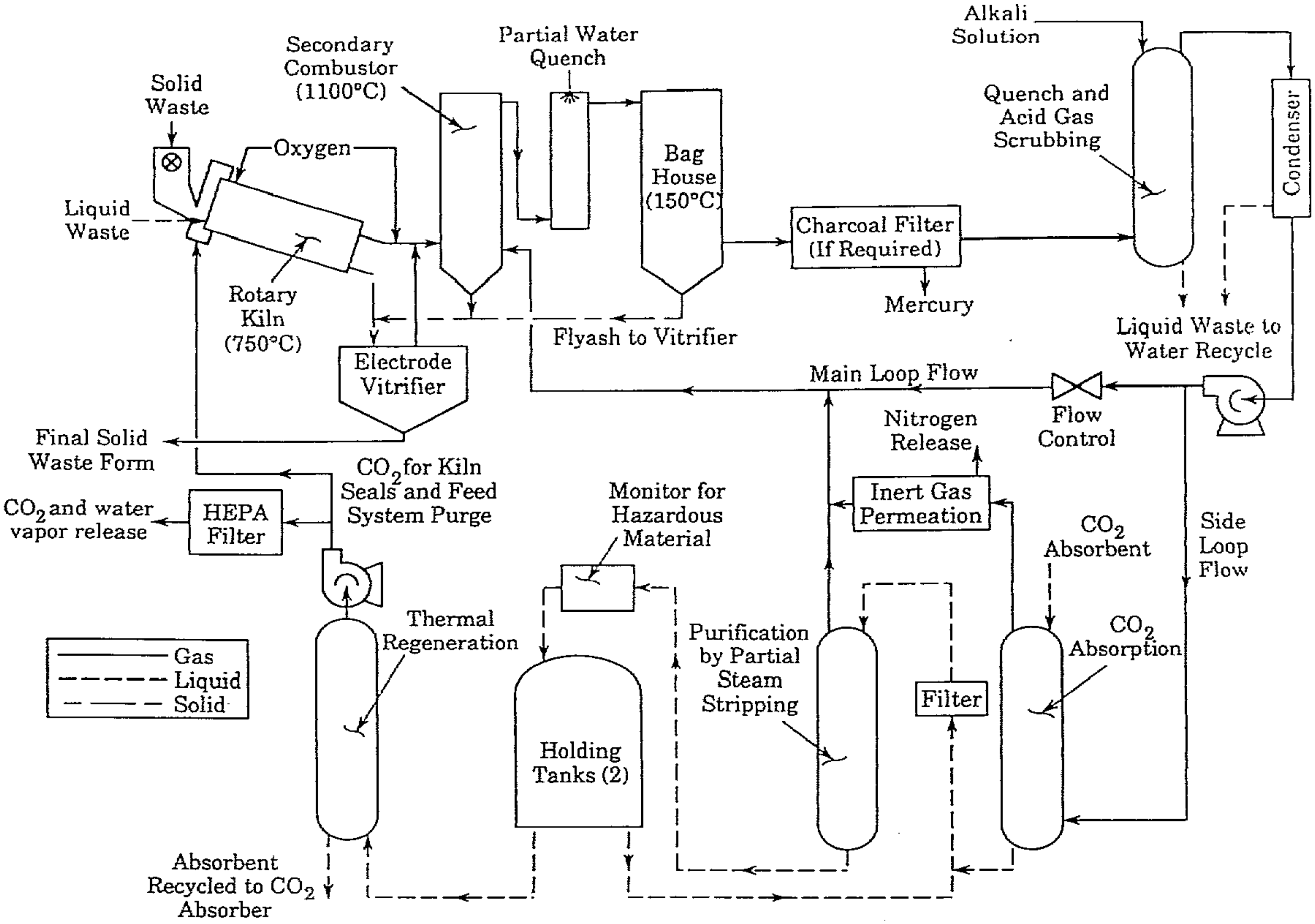

Figure 9: Closed-loop process for incineration and vitrification of hazardous waste.

of submicron particles and fume solids that are difficult to collect [17, 18]. These devices also must be sealed at the waste material feed point and the slag removal area to prevent the release of small particulates and volatiles.

With all combustor types, oxygen should be controlled by maintaining a minimum O_2 level in the recirculated gas flow or the gas that exits the combustor. Combustion temperature can be separately controlled by varying the waste-feed rate or the recirculation rate of the closed-loop gases, or by cooling the closed-loop gases.

Figure 9 shows a closed-loop process for incineration and vitrification of hazardous and mixed wastes. The system would be able to process a large throughput of waste materials without the need for extensive sorting and characterization. Thermal treatment devices include a rotary kiln, electrically heated or gas-fired vitrifier and a secondary combustor.

Conclusion

Thermal treatment of hazardous and mixed wastes in a closed-loop off-gas treatment system will allow direct oxidation to be a viable option. Facilities for storage of hazardous and mixed wastes are becoming less available. Restrictions are also being imposed on the transportation of these wastes. In the AST process, CO_2, acid gases, and contamination from closed-loop incineration processes are removed in a side loop. An aqueous solution of potassium carbonate was selected as the preferred absorbent due its tolerance for waste off-gas streams containing oxygen, unburned organics, and acid gases. Contaminants do not significantly affect absorbent performance, and hazardous and radioactive materials can be detected and removed during the purification and regeneration process. With a closed-loop off-gas system incineration can be an acceptable option for disposal of hazardous and mixed wastes.

Acknowledgments

Work at ANL to develop closed-loop thermal-treatment processes has been supported by Laboratory Directed Research and Development funds and by ANL Waste Management. The work was performed under DOE Contract No. W-31-109-Eng-38.

Notation

ANL	Argonne National Laboratory
AST	absorbent solution treatment

FTIR	Fourier transform infrared spectrometer
HEPA	high efficiency particulate air [filters]
MEA	monoethanolamine

References

[1] P.A. Nelson and W. M. Swift. Thermal and chemical remediation of mixed waste. U.S. Patent No. 5,335,609, Aug 1994. Patent Cooperation Treaty Extension filed April 21, 1994.

[2] P.A. Nelson and W.M. Swift. Unvented thermal process for treatment of hazardous and mixed wastes. In *Proceedings of the 1993 Incineration Conference*, pages 671–678. Knoxville, TN, May 1993.

[3] C. R. Brunner. *Hazardous Waste Incineration*. McGraw Hill, Inc., second edition, 1993.

[4] E. P. Zbacnik and T. M. Brookes. Bulk CO_2 removal from flue gas. In *New Technologies for Air Pollution Reduction*. The Royal Society of Chemistry, London, UK, May 1991.

[5] S. A. Rushing. CO_2 recovery improves cogen plant economics. *Power Engineering*, 46–47, Apr 1994.

[6] R. Barchas and R. Davis. The Kerr-McGee/ABB Lummus crest technology for the recovery of CO_2 from stack gases. *Energy Conversion Management*, 33(5-8):333–340, 1992.

[7] M. T. Sander and C. L. Mariz. The Fluor Daniel ECONOMINE FG process: past experience and present day focus. *Energy Conversion Management*, 33(5-8):341–348, 1992.

[8] M. A. Wilson, R. M. Wrubleski, and L. Yarborough. Recovery of CO_2 from power plant flue gases using amines. *Energy Conversion Management*, 33(5-8):325–331, 1992.

[9] A. L. Kohl and F. C. Riesenfeld. *Gas Purification*. Gulf Publishing Company, fourth edition, 1985.

[10] R. K. Bartoo. Removing acid gas by the Benfield process. *Chemical Engineering Progress*, 46–47, Oct 1984.

[11] K. F. Butwell, D. J. Kubek, and P. W. Sigmund. Alkanolamine treating. *Hydrocarbon Processing*, Mar 1982.

[12] B. S. Grover and E. L. Bergen. CO_2 recovery from flue gas by the Benfield process. In *Petro-Energy '83*. Houston, TX, Sep 1983.

[13] F. Hetzler, J. Feldman, and M. Trichon. Incineration of ion exchange resins: a mixed waste. In *Proceedings of 1994 Incineration Conference*, pages 105–108. Houston, TX, May 1994.

[14] D. M. Stull, B. W. Logsdon, and J. J. Pellegrino. *An Investigation of Gas Separation Membranes for Reduction of Thermal Treatment Emissions*. Technical Report US. DOE/OSTI-4500-R75, EG&G Rocky Flats, Inc., May 1994.

[15] Z. Mao, J. C. Demirgian, and G. Reedy. Evaluation of a Fourier transform infrared continuous emission monitor field test at a TSCA incinerator. In *Proceeding of 1994 Incineration Conference*, pages 55–62. Houston, TX, May 1994.

[16] M. Ho, R. H. Sawyer, J. P. Stumbar, and J. M. Perdek. Long-term field demonstration of the Linde oxygen combustion system installed on the EPA mobile incinerator. In *EPA Fifteenth Annual Research Symposium*. Cincinnati, OH, Apr 1989.

[17] J. W. Ruffner, T. Rivers, and R. A. Koenig. Meeting ALARs with an improved emissions control system for the plasma arc centrifugal treatment system. In *Proceedings of 1994 Incineration Conference*, pages 671–677. Houston, Texas, May 1994.

[18] H. I. Hollander, A. L. Plumley, R. S. DeCesare, and D. A. Hoecke. ASME/US Bureau of Mines investigative program on vitrification of combustion ash/residue – findings and conclusions. In *Proceedings of 1994 Incineration Conference*, pages 621–631. Houston, Texas, May 1994.

Received: October 1, 1994
Accepted: October 2, 1995