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Mixed Waste Focus Area Alternative Oxidation Technologies Development and Demonstration Program

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ABSTRACT

The Mixed Waste Focus Area (MWFA) is currently supporting the development and demonstration of several alternative oxidation technology (AOT) processes for treatment of combustible mixed low-level wastes. The impetus for this support derives from regulatory and political hurdles frequently encountered by traditional thermal techniques, primarily incinerators. AOTs have been defined as technologies that destroy organic material without using open-flame reactions. Whether thermal or nonthermal, the processes have the potential advantages of relatively low-volume gaseous emissions, generation of few or no dioxin/furan compounds, and operation at low enough temperatures that metals (except mercury) and most radionuclides are not volatilized. Technology development and demonstration are needed to confirm and realize the potential of AOTs and to compare them on an equal basis with their fully demonstrated thermal counterparts.

AOTs include both thermal and nonthermal processes that oxidize organic wastes but operate under significantly different physical and chemical conditions than incinerators. Nonthermal processes currently being studied include Delphi DETOX and acid digestion at the Savannah River Site, and direct chemical oxidation at Lawrence Livermore National Laboratory. All three technologies are at advanced stages of development or are entering the demonstration phase. Nonflame thermal processes include catalytic chemical oxidation, which is being developed and deployed at Lawrence Berkeley National Laboratory, and steam reforming, a commercial process being supported by Department of Energy. Related technologies include two low-flow, secondary oxidation processes (Phoenix and Thermatrix units) that have been tested at MSE, Inc., in Butte, Montana. Although testing is complete on some AOT technologies, most require additional support to complete some or all of the identified development objectives. Brief descriptions, status, and planned paths forward for each of the technologies are presented.

BACKGROUND

Alternative oxidation technologies (AOTs) fundamentally are alternatives to excess air combustion (incineration). The primary impetus for development and deployment of AOTs is public opposition to emissions generated by thermal technologies in general and incinerators in particular. Stakeholders [1] have expressed concerns with

- incinerator releases of products of incomplete combustion, products of recombination (especially dioxins and furans), and emission of toxic metals and radionuclides;
- the quantity of offgas released from waste treatment operations (processes that generate relatively lower offgas volumes are perceived as intrinsically more desirable);
- treatment operation excursions that could lead to uncontrolled releases to the environment; and
- formation of dioxins and furans during cooling of high-temperature offgases.

Additional stakeholder principles relevant to development and deployment of AOT processes are found in the Department of Energy (DOE) summary of comparative results for nonthermal and thermal systems [2]. A composite of these concerns and principles provided the foundation for the Mixed Waste Focus Area (MWFA) AOT program.

Site support for operational deployment of these technologies is another vital element of development justification. Lawrence Livermore National Laboratory (LLNL) is currently using direct chemical oxidation (DCO) to dispose of a chlorinated solvent waste stream. The Savannah River Site (SRS) has provided a letter of

commitment indicating support for acid digestion as treatment for significant ^{238}Pu and highly enriched uranium waste streams. Lawrence Berkeley National Laboratory (LBNL) is using the catalytic chemical oxidation (CCO) process to treat tritium-contaminated mixed wastes.

The anticipated promulgation of the Maximum Achievable Control Technology rule also provides motivation for the development of AOTs. The DOE has determined that the three existing incinerators may require substantial modification to comply with rule provisions; trial burns will be conducted at the third unit to determine compliance capability. AOTs are expected to more readily meet the more stringent emission standards for dioxins/furans, HCl and Cl_2 , CO, and total hydrocarbons.

The anticipated primary AOT use is niche waste treatment applications involving particularly difficult radionuclides, e.g., tritium or actinides, or problematic hazardous chemical contaminants. AOTs also may be deployed for treatment of low-volume, continually generated mixed waste streams to avoid problems associated with accumulation, storage, and compliance logistics. AOTs could alleviate compliance pressures on and related modification expenditures for DOE incinerators by providing an alternate treatment route for problematic waste constituents or by reducing total offgas emissions through use of low-flow secondary combustion chambers. Ongoing and planned demonstrations of the several AOT technologies should serve to better define respective deployment roles in the overall mixed waste treatment arena.

The justification for development studies arises from the need to enhance the effectiveness and operational reliability of AOTs. Few of these technologies have been tested through the pilot demonstration phase. Those that have been demonstrated tend to be the less aggressive technologies that have niche applications for a few waste streams with limited volume. To supplant incineration, the more aggressive and broadly applicable treatment technologies require development and demonstration to determine waste processing capability, waste handling and acceptability concerns, materials corrosion issues, and offgas characteristics and to minimize and characterize secondary wastes, resolve radioactivity containment issues, and define acceptable final waste forms. The overall cost effectiveness of the processes must be determined at the advanced development and demonstration stages, or gates.

In the following sections, MWFA-supported AOTs are briefly described together with their status and plans for each technology.

NONTHERMAL AOT PROCESSES

Delphi DETOX

The DETOX process (Fig. 1), which was developed by Delphi Research, Inc. of Albuquerque, New Mexico, is a catalytic, aqueous process that oxidizes organic materials with internal regeneration of the oxidant [3]. The low operational temperature (150–250°C) and the nature of the catalyst typically do not produce regulated gases or volatile metals in the offgas. The reagent solution (containing FeCl_3 with Pt and Ru co-catalysts) is not consumed in the reaction, readily dissolves metals, and therefore can accumulate toxic and radioactive metals before recovery or disposal. Oxygen present above the reagent solution supports reoxidation of the reduced ferrous ions back to ferric:



Reported destruction efficiencies range from better than 99.999% for nonchlorinated solvents to 98.9% for polychlorinated biphenyl compounds. The process, which operates at low to moderate pressures (20–200 psig), is generally more applicable to liquid wastes, but it can accept some solids, limited by solubility of the inert matrix in the working fluid.

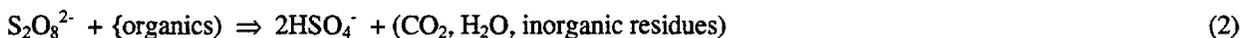
The MWFA-supported project provides for a prototype demonstration of this process using hazardous waste feed stock at an estimated throughput of 25 kg (dry weight organic) per hour. The final phase of testing, which is to be completed by August 1, 1998, includes testing with (1) oil and wastewater with oil, (2) oxidizable solids (debris), (3) organic sludges, (4) chlorinated solvents, and (5) scintillation fluids and Trimsol.

The developers anticipate that application of the DETOX process may range from small, portable units to large, stationary systems. A 190-L vessel should be capable of oxidizing 5–25 kg of hazardous organics per hour. Larger, stationary units are projected that could be capable of processing wastes in the ton-per-hour range.

Figure 1 here

Direct Chemical Oxidation

The DCO process, developed at LLNL, is a nonthermal, ambient pressure, aqueous based technology for the oxidative destruction of the organic components of hazardous or mixed waste streams [4]. The process uses solutions of peroxydisulfate salts (typically sodium or ammonium) to mineralize the organics to carbon dioxide and water, and the expended oxidant may be regenerated electrolytically to minimize secondary waste. The net waste treatment reaction is



The peroxydisulfate process is an application of a well-established industrial technology. Acidified ammonium peroxydisulfate is one of the strongest oxidants known, exceeded only in oxidative power by fluorine, ozone, and oxyfluorides. The oxidation potential of peroxydisulfate is high enough to oxidize nearly all organics, and thus, the process is virtually "omnivorous." Many organics are oxidized by the process at ambient pressure and temperatures in the 80–100°C range; more resistant materials, e.g., polyvinyl chloride polymer require thermal pretreatment (140–180°C for 24 h) before oxidation by peroxydisulfate.

An integrated bench-scale system for the destruction of a wide range of chlorinated organic liquids and organic-contaminated sludges has been demonstrated at LLNL. Many chlorinated solvents require hydrolysis to offset difficulties presented by their high volatility and low solubility in water. This first-step hydrolysis reaction takes place at elevated temperatures in a sealed reactor. The resultant products, generally more soluble and less volatile, then are mineralized in the DCO process. This integrated system is shown in Fig. 2.

The integrated DCO process has been demonstrated on LLNL waste streams containing chlorinated solvents. Approximately 300 kg of low-level waste containing mixed chlorosolvents have been processed. In both industrial applications and the LLNL tests, a broad spectrum of materials has been oxidized successfully using peroxydisulfate, including acetic acid, formamide, ethylene glycol, tributyl phosphate, methyl chloroform, carbon tetrachloride, and carbon residuals found in incinerator ash. LLNL is pursuing commercialization of the process through a collaborative effort with a waste treatment vendor.

The primary function of DCO technology is oxidative destruction of a broad spectrum of organic solids and liquids. This includes solvents; detergents; pesticides; water-insoluble oils and greases; charcoal filter media; incinerator chars and tars; paper; plastics (except fluorinated polymers); chlorinated, sulfated, and nitrated wastes; and organics mixed with organic/inorganic matrices such as soils, sands, or sludges. Solutions of the oxidant can be used to treat inaccessible wastes (such as organics within radioactively contaminated machinery or gloveboxes) and in decontamination or destruction of chemical warfare agents, explosives, and propellants. Because ammonium peroxydisulfate can be stored almost indefinitely at room temperature, the process of waste destruction can be decoupled in time and place from generation of the peroxydisulfate oxidant. The process is readily scalable from a transportable, bench-scale size to large, stationary units.

Figure 2 here

Acid Digestion

The acid digestion technology, which was developed at SRS, is a nitric-phosphoric acid, wet oxidation technology capable of destroying organic compounds, including paper, plastics, resins, and munitions [5,6]. The technology uses an admixture of an oxidant (nitric acid) and a carrier (phosphoric acid). The phosphoric acid supports the retention of nitric acid in solution at an atmospheric pressure well above its normal boiling point. The oxidation of organic compounds usually is initiated by the production of organic radicals generated by dissolved NO_2 and NO in solution, e.g.,



The process routinely operates in the 130–180°C range at atmospheric pressure; however, slightly higher temperature and pressure are required to oxidize more resistant plastics. Oxidation rate is rapid (a few minutes) for less stable compounds (paper, munitions) but slower (up to an hour) for some plastics. Metals and most radionuclides are retained in solution after destruction of organic materials. Treated waste residues from the process are immobilized readily by using either a low-temperature magnesium phosphate ceramic or a high-temperature iron phosphate glass.

The acid digestion process flow sheet is shown in Fig. 3. Many different organic compounds have been oxidized to water and carbon dioxide in the 130–150°C range at low pressures (0–5 psig). Polystyrene ion exchange resins have been effectively destroyed at 175°C and 5–10 psig. More stable compounds such as polyethylene have been decomposed below 200°C and 10 psig. NO and NO₂ can be recovered using hydrogen peroxide, resulting in NO_x emissions well below 100 ppm. Stabilization can be attained by several methods, but immobilizing the phosphoric acid residue as magnesium phosphate ceramic has been shown to pass the TCLP test.

Core technologies of the acid digestion process have been demonstrated successfully in the laboratory in both 2-L and 40-L reaction systems. Studies are on-going in areas of mixed organic feed destruction and oxidant recycle. Acid digestion is an identified candidate for oxidative treatment of large volumes of ²³⁸Pu job control wastes at SRS. The technology has been made commercially available through a licensing agreement with a waste treatment vendor.

Figure 3 here

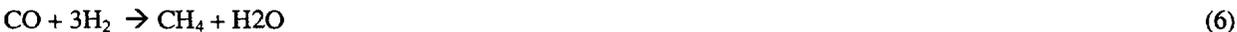
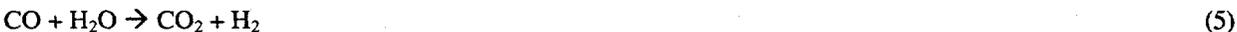
THERMAL AOT PROCESSES

Steam Reforming

The DOE is supporting demonstration of steam reforming treatment of mixed wastes under contract with ThermoChem Inc. and its subcontractors. The nominal throughput of the demonstration is 90 lb/h of various low-level mixed waste surrogates [7]. Steam reforming is a versatile process that destroys organic materials through reactions with steam:



CO then reacts further with steam and hydrogen:



In addition to destroying organics, steam reforming can destroy inorganic nitrates, and this process retains many radionuclides in the reformer bed because of the relatively low operating temperature. The steam reforming process usually involves two stages: (1) waste is pyrolyzed and volatilized by exposure to steam at elevated temperatures (300–800°C) and (2) volatile species are further reacted with steam at temperatures up to 1200°C to produce synthesis gas.

The ThermoChem process (shown in Fig. 4) gasifies organic waste at 550–600°C in a fluidized bed of sodium carbonate (or some other starting bed selected to yield a desirable end product) that serves as catalyst for reforming reactions. After particulate removal, the product gases from the steam reformer flow into a Thermatrix flameless thermal oxidizer that converts volatiles to water, carbon dioxide, and acid gases. An offgas cleanup system removes the acid gases as dry salts; a baghouse and HEPA filter remove particulate before discharge to the environment.

Recent test runs with simulated mixed wastes containing uranium and a PCB simulant indicated that heavy metals are retained in the first-stage reactor bed and destruction/removal efficiencies (DREs) of 99.9999% have been demonstrated. Follow-on efforts include detailed design and costing for a 500-lb/h system for testing with radioactive waste.

Figure 4 here

Catalytic Chemical Oxidation

The CCO technology, which was developed by LBNL, is a high-temperature, non-flame process that decomposes organic chemicals in the presence of alumina pellets and platinum-coated alumina pellets as catalysts [8]. The primary focus at LBNL is treatment of tritiated mixed waste. Research institutions conducting life science and biomedical studies and the pharmaceutical industry invariably produce mixed waste containing tritium and other radioisotopes. Currently, there is no satisfactory disposal route for tritiated mixed waste of high specific activity. Disposal options exist for radioactive wastes; therefore, the objective of CCO treatment is efficient conversion of hazardous organics contained in the tritiated wastes. Before this application, the technology had been applied successfully to destruction of hazardous organic chemicals for remediation projects. In reality, the technology is an extension of catalytic conversion technology used in the automotive industry. The LBNL process can accommodate and treat both organic and aqueous mixtures to a 99.999% DRE.

The CCO process, shown in Fig. 5, consists of a preheater, an oxidation chamber, a heated packed-bed reactor filled with catalyst pellets, and an emission reduction device. The entire assembly is contained in a glovebox enclosure. The operating temperature of the catalytic oxidation unit is in the 450–750°C range. During treatability studies, LBNL is constrained to process no more than 10 kg of liquid tritiated waste per year. At the maximum proposed flow rate, processing rates of approximately 1 L/day are feasible. DREs in excess of 99.999% have been demonstrated successfully with surrogate and actual mixed waste samples. The recovered tritium will be recycled; final disposition of the oxidation products will be determined by the outcome of a Delisting Petition.

Figure 5 here

ALTERNATIVE SECONDARY OXIDATION TECHNOLOGIES

Although they do not rigorously conform to the definition of AOTs, the MWFA has supported test demonstrations of a number of low-flow combustion devices as alternatives to conventional secondary combustion chambers. Two devices, the Thermatrix oxidizer and the Phoenix Low-Flow Secondary Combustion Chamber (LFSCC) are electrically heated units that significantly reduce the total volume of treatment effluents by eliminating the natural gas or propane heat source. Both devices were demonstrated at the MSE Technology Applications, Inc., offgas test bed located in Butte, Montana [9].

The Thermatrix flameless oxidizer [10] originally was developed to treat process streams lean in combustible components. It operates by supplying sufficient temperature, very efficient mixing, and adequate oxygen to the input gas stream; the exit temperature is maintained at 850–900°C. The process gas first encounters ceramic spheres that distribute and mix it. Downstream from the spheres are heated ceramic saddles that provide the heat and residence time to ignite and oxidize the organic content. Tests conducted by introducing organics in concentrations up to 1000 ppm produce DREs of 99.998% for CCl₄ and 99.99% for benzene.

The Phoenix LFSCC consists of two subsystems—a high heat flux electric heater and a holding chamber. The electric heater is enclosed in a 0.5-m-diam pipe section approximately 1.5 m long. The heater is designed to raise the entering gas temperature to 1100°C. The holding chamber is a refractory-lined cylinder 1.25 m in diameter and 1.2 m high. Two concentric ducts within the holding chamber route the gas through annular flow paths, reversing directions twice before exiting the chamber. The labyrinth design is intended to hold the heated gas stream for at least 2 s before exhaust. Demonstration testing of the Phoenix LFSCC indicated 99.99% DRE for trichloroethane, chloroform, and benzene was attained.

The Thermatrix and Phoenix oxidizers are intended to serve as secondary combustion chambers to alternative oxidation primary units, such as the steam reforming process, or can be used in sequence with more conventional primary oxidation devices. Either unit would decrease the total gaseous effluent from the treatment system substantially. Demonstration data developed by the MWFA at the MSE TA, Inc., facilities provides end-users with valuable performance and operational experience data.

CONCLUSIONS

The MWFA has supported and is supporting development/demonstration of several promising AOTs, principally in response to stakeholder concerns regarding thermal processing technologies. Despite the emergent nature of these technologies, each has shown significant promise in the treatment of a variety of mixed wastes. The described technologies represent potential solutions to a broad spectrum of combustible mixed waste treatment problems, and although it appears that these processes will not be as omnivorous as incineration or high-temperature plasma technologies, individual processes are likely to find successful niche applications. Sites having small volumes of problematic combustible organics or mixed waste containing high levels of particularly troublesome radioisotopes, e.g., plutonium or tritium, should consider possible use of an alternative oxidation technology for treatment to meet land disposal requirements. Similarly, those sites experiencing stakeholder opposition to thermal processing or having adopted a policy excluding thermal processing of radioactive or mixed may discover treatment options among these less aggressive technologies. The MWFA is actively seeking deployment opportunities among these emerging technologies and has dedicated resources to establish interfaces between the principal investigators and end users. Continued development and demonstration and increasing deployment of AOTs are anticipated as an important tool in the reduction of DOE's mixed low-level waste inventory.

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Figure Captions

Fig. 1.. DETOXSM Wet Oxidation Process.

Fig. 2. Process Flow Diagram for DCO Integrated system.

Fig. 3. Acid Digestion Process Flow Diagram.

Fig. 4. ThermoChem Inc. Steam Reforming Process.

Fig. 5. The National Tritium Labelling Facility (LBNL) Tritiated Waste Oxidation System (CCO-2).

DETOXSM WET OXIDATION PROCESS

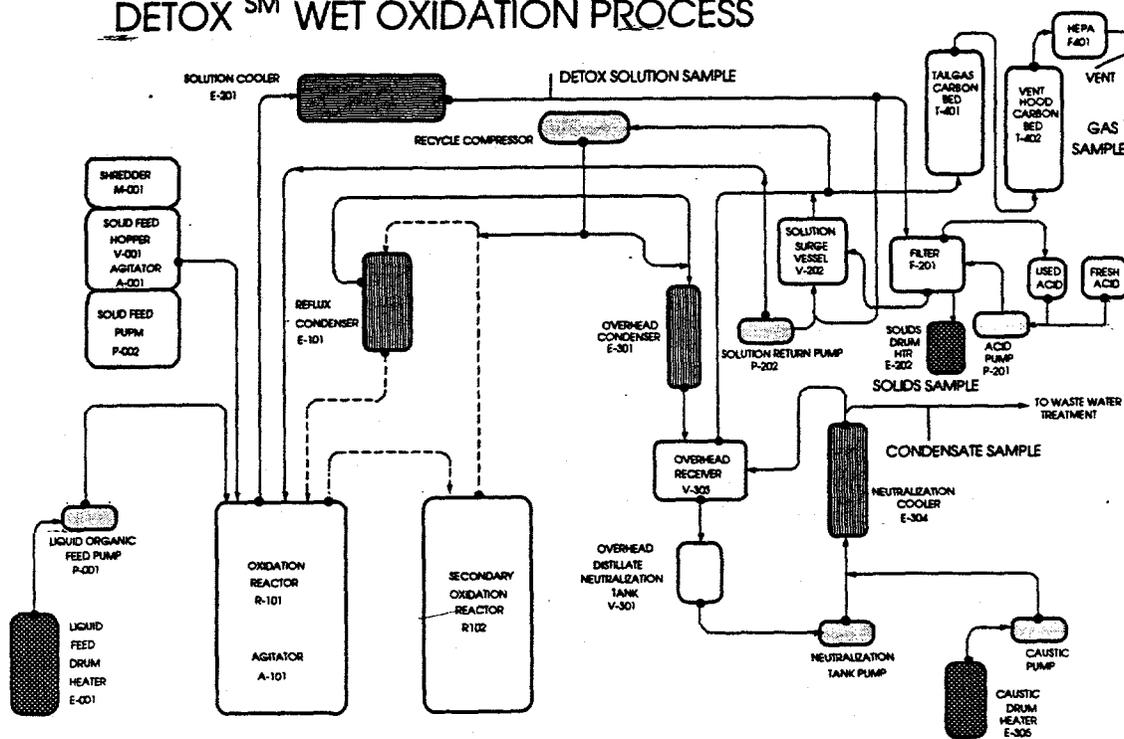


Figure 1

Process Flow Diagram For DCO Integrated System

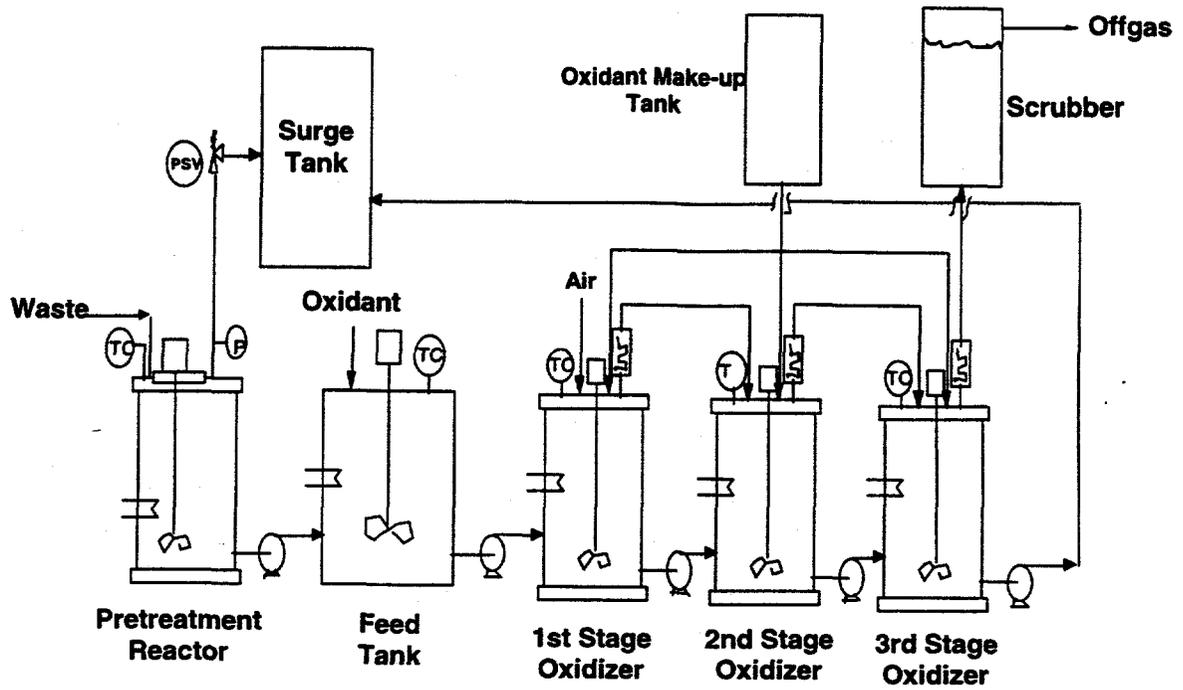


Figure 2

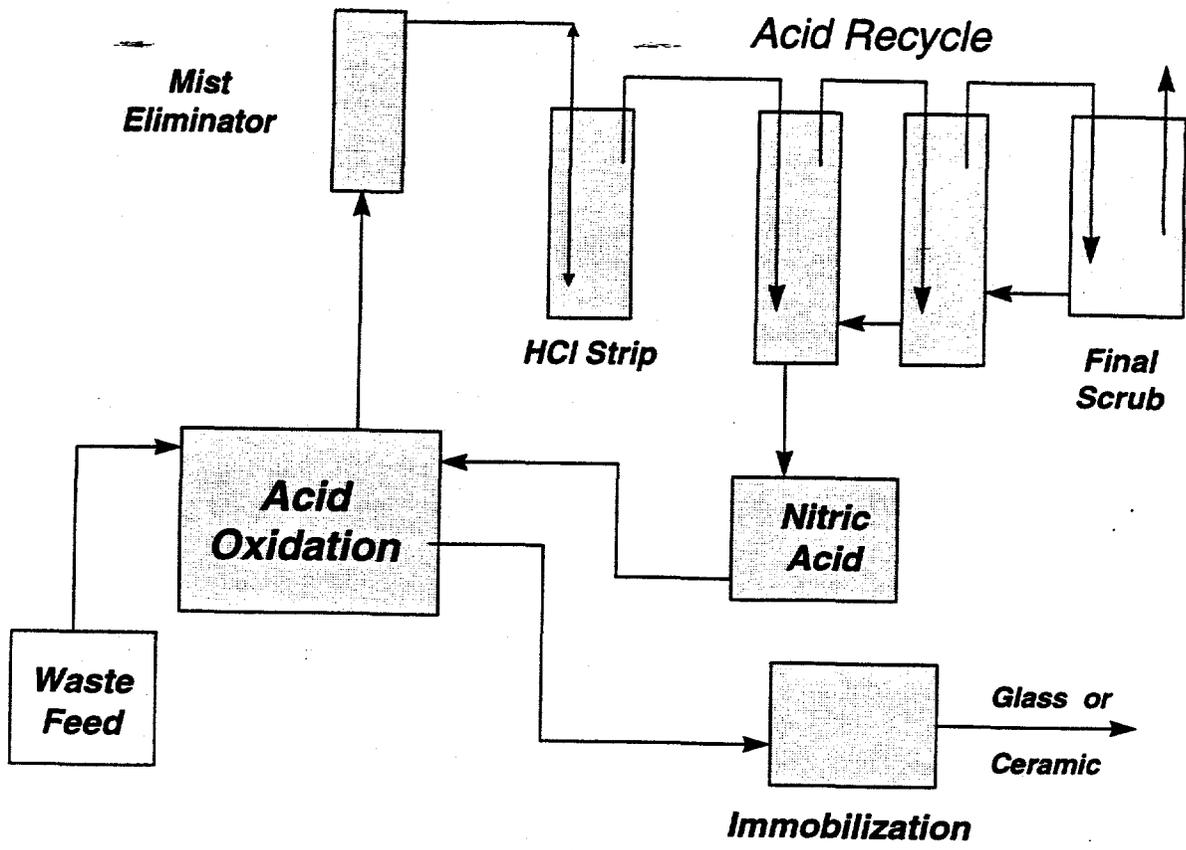


Figure 3

Low Level Mixed Waste

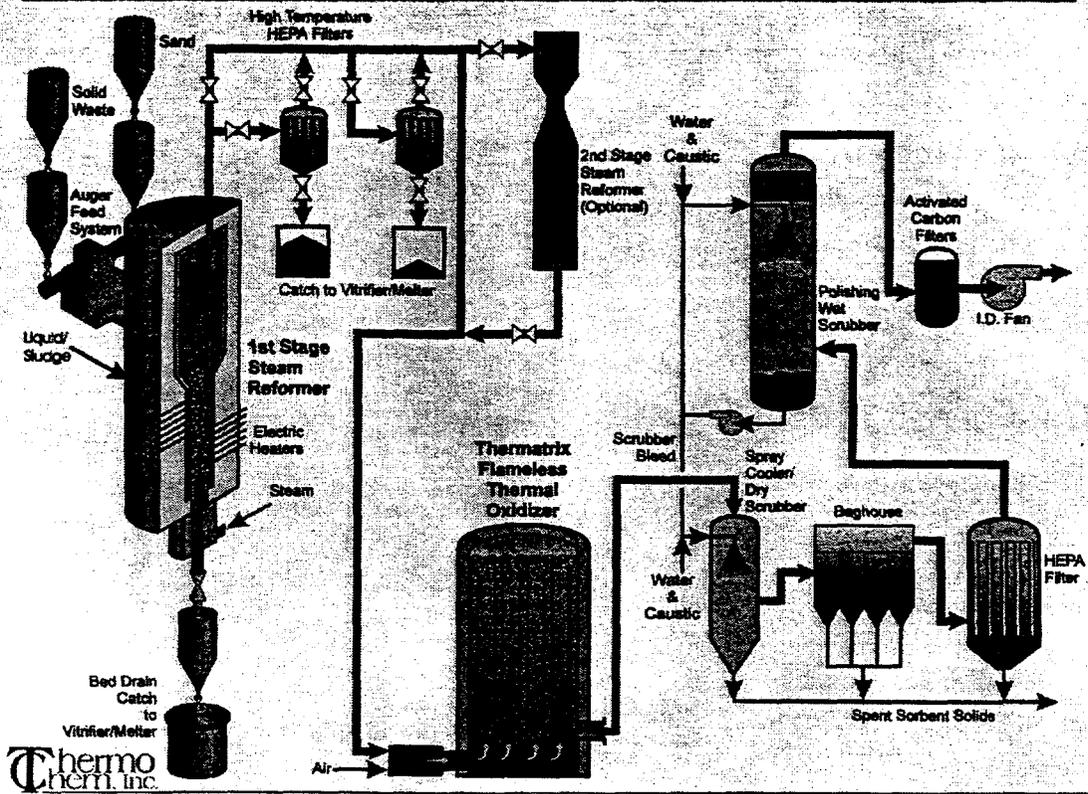


Figure 4

The National Tritium Labelling Facility (LBNL)
Tritiated Waste Oxidation System (CCO-2)

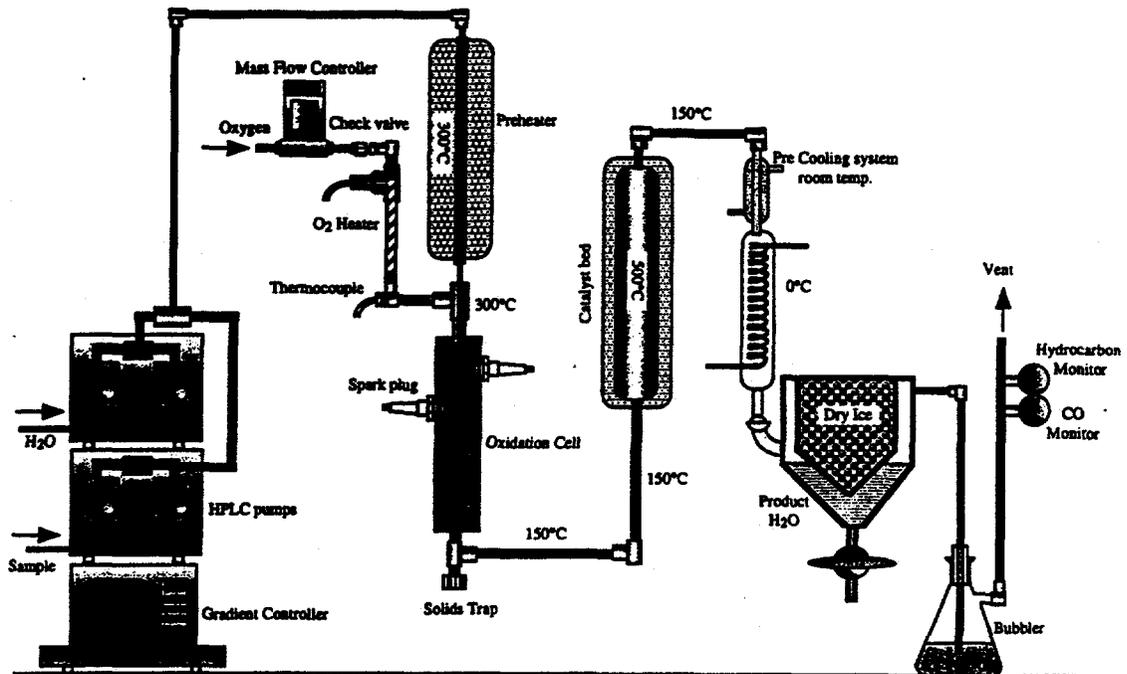


Figure 5