Conf-950216--56

DOE/MC/29107-95/C0412

ENGINEERING DESIGN AND TEST PLAN FOR DEMONSTRATING DETOX^{SM} TREATMENT OF MIXED WASTES

Authors:

Scott Goldblatt
Patrick Dhooge

Contractor:

Delphi Research, Inc.
701 Haines Avenue, NW.
Albuquerque, New Mexico 87102

Contract Number:

DE-AC21-92MC29107

Conference Title:

WM '95 HLW, LLW, Mixed Wastes and Environmental Restoration-Working Towards a Cleaner Environment

Conference Location:

Tucson, Arizona

Conference Dates:

February 26 to March 2, 1995

Conference Sponsor:

The University of Arizona, American Nuclear Society, U.S. DOE, New Mexico State University and the Waste-Management Education and Research Consortium (WERC), and the American Society of Mechanical Engineers.

- disclaimer inside -

MASTER

plc

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

This report has been reproduced directly from the best available copy.

Available to DOE and DOE contractors from the Office of Scientific and Technical Information, 175 Oak Ridge Turnpike, Oak Ridge, TN 37831; prices available at (615) 576-8401.

Available to the public from the National Technical Information Service, U.S. Department of Commerce, 5285 Port Royal Road, Springfield, VA 22161; phone orders accepted at (703) 487-4650.

ENGINEERING DESIGN AND TEST PLAN FOR DEMONSTRATING DETOX^{SM} TREATMENT OF MIXED WASTES

Scott D. Goldblatt and Patrick M. Dhooge, Delphi Research, Inc.

ABSTRACT

DETOX^{SM} is a cocatalyzed wet oxidation process in which the catalysts are a relatively great concentration of iron ions (typically as iron(III) chloride) in the presence of small amounts of platinum and ruthenium ions (1,2). Organic compounds are oxidized completely to carbon dioxide, water, and (if chlorinated) hydrogen chloride. The process has shown promise as a non-thermal alternative to incineration for treatment and/or volume reduction of hazardous, radioactive, and mixed wastes (3-5).

Design and fabrication of a demonstration unit capable of destroying 25. Kg/hr of organic material is now in progress. This paper describes the Title II design of the demonstration unit, and the planned demonstration effort at Savannah River Site (SRS) and Weldon Spring Site Remedial Action Project (WSSRAP).

BACKGROUND

Oxidation of materials in the DETOX^{SM} process is at present conducted in a stirred tank containing an acidic (3. - 4.% HCl) aqueous solution of the cocatalysts at temperatures of 400. - 473. K. System operating pressure ranges from atmospheric at 400. K to approximately 700. kPa at 473. K. Organic compounds are oxidized in the catalyst solution by iron(III) ions. In the oxidation process, iron(III) is reduced to iron(II). Oxygen introduced into the solution oxidizes iron(II) back to iron(III). Figure 1 illustrates the process.

Place Figure 1 Here

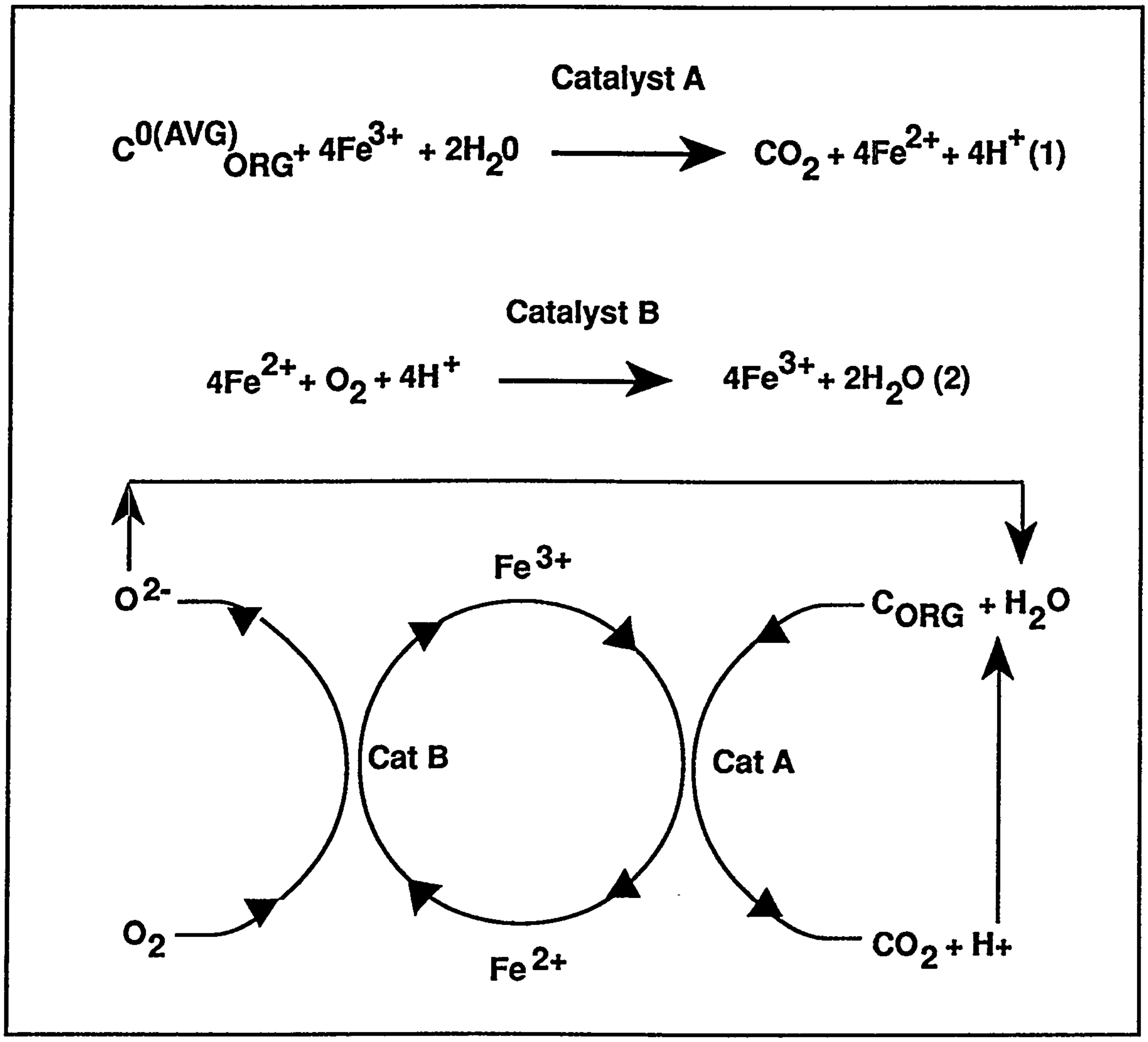
Laboratory tests have determined the apparent rate constants and activation energies for oxidation of a wide variety of organic materials, including cellulosic materials, hydrocarbon oils, chlorinated and non-chlorinated aromatic and aliphatic solvents, energetic compounds, plastics, and chlorinated aromatic compounds such as polychlorinated biphenyls (PCBs). Measured rates indicate that at a temperature of 423. K approximately 0.5 to 10. moles/L-hr of organic material can be destroyed at organic material/catalyst solution contact areas of 300. to 6000. cm^2/L.

There are many low level and mixed wastes which are organic in nature and could be treated using DETOX^{SM} as an alternative to incineration. Mobile treatment units could be used to destroy the organic components of wastes on site, thus eliminating the costs and concerns of transportation and other forms of disposal. Heavy and radioactive metals remain in the DETOX^{SM} process solution. The process solution can be converted to an iron oxide residue by boiling off HCl, and the residue stabilized for ultimate disposal.

TITLE II DESIGN

Design Basis

A site selection evaluation was conducted in parallel with the start of Phase II design. Ten (10) DOE sites were considered as possible demonstration sites due to the types of wastes available for the demonstration effort. The list was reduced to seven sites based on expressions of interest, and these seven sites were ranked according to evaluation criteria provided by the DOE. The



Catalyst A

$$C^{0(AVG)}_{ORG} + 4Fe^{3+} + 2H_20 \longrightarrow CO_2 + 4Fe^{2+} + 4H^{+} (1)$$

Catalyst B

$$4Fe^{2+} + O_2 + 4H^{+} \longrightarrow 4Fe^{3+} + 2H_2O (2)$$

Fig. 1: DETOX Process Chemistry

two most highly ranked sites, Savannah River Site (SRS) and Weldon Spring Site Remedial Action Project (WSSRAP), were recommended for the proposed demonstration. The wastes at these sites helped define the requirements for the demonstration unit.

Waste types available for the demonstration include high and low boiling organic liquids (including chlorinated solvents), some paint sludges and similar solids, tributyl phosphate, and polychlorinated biphenyl (PCB)-contaminated liquids. For the purposes of mass and energy balance calculations, three organic compounds were chosen which would represent compositions typical of the range of waste types in the demonstration. These were a completely saturated aliphatic hydrocarbon (i.e., $-CH_2-$), tributyl phosphate, and a PCB having 60.% by weight chlorine content.

Further requirements for the demonstration unit were provided in discussion with DOE EM-50 representatives. The requirements were for the most versatile unit possible consistent with a reasonable cost. It was decided in these discussions that the unit would have a method of feeding both liquid and solid organic materials to the reaction vessel and that the unit would have a system for semi-continuous removal of inert particulates or particulates generated during waste processing. These features at least doubled the unit size and cost over a liquid-only unit without solids removal, but it was felt important to demonstrate as wide a range of waste treatment ability as reasonably possible. Transportability of the demonstration unit was also an important consideration in design.

After consideration of the types and amounts of wastes at the demonstration sites, and particularly at WSSRAP, in combination with what was considered a reasonable throughput consistent with unit size and cost, a nominal capacity of 25. kg/hr was chosen for the demonstration unit. Once the reaction vessel is at temperature, the unit will operate 24. hrs per day.

Critical issues in the design effort were: operator and environmental safety and health; process effluents of minimum environmental concern; and ability to achieve the planned capacity.

Special considerations in the design effort were: modularity and transportability of the demonstration unit; ability to treat both liquid and solid waste materials; ability to remove solids from the process solution during waste treatment; design conformance with demonstration site requirements; compatible materials of construction for components contacting the process solution or its vapors; and secondary or tertiary containment in critical areas.

The design effort also took into account the requirements of 40 CFR Parts 264 and 265, the OSHA Standards for General Industry, 29 CFR Part 1910, and all applicable sections of DOT regulations, 49 CFR.

Title II Design Format

Jacobs Applied Technology (JAT), a subsidiary of Jacobs Engineering Group (JEG), was chosen for the Title II design effort due to JAT's extensive experience in modular chemical process design and construction, the resources and experience in chemical process design and environmental applications which were available through JEG, and the estimated cost and schedule for designing and constructing the unit.

The Title II design effort was conducted in a logical progression of preliminary PFD and P&ID preparation and review, revised PFD and P&ID preparation and review, HAZOP review, final review, and construction cost estimate.

Title II Design

PFD

Figure 2 is the final PFD for the demonstration unit. Flows 1 and 2 are liquid and solid organic feeds to the reaction vessel. Flow 3 is oxygen feed to the reaction vessel. Flow 4 is product gas and water vapor exiting the reaction vessel, and flow 5 is water return to the reaction vessel from the reflux condenser. The reflux condenser serves to reduce the amount of water vapor in the product gases to the overhead condenser, provide some cooling for the reaction vessel (the reaction vessel is also cooled with an oil-filled jacket), and knock down any heavy organics in the product gases. Flow 6 is product gas to the overhead condenser, and flow 7 is condensed water to a receiver tank. Flows 20 and 21 are product gas, which contains a small amount of excess oxygen, through a carbon bed and to vent. Analyzers for oxygen, carbon dioxide, volatile organic compounds, HCl, and radiation are on the product gas lines.

Place Figure 2 Here

In order to remove inert solids or inorganic solids formed during treatment of organics, a flow of process solution is taken from the reaction vessel, cooled, filtered, and returned to the vessel. Flows 8 and 9 are process solution through a solution cooler and to the filter. Flows 10 and 11 are filtered process solution to a surge tank and returned to the reaction vessel. Flow 12 is solids removed from the process solution, which have been rinsed thoroughly and are fed into a drum for stabilization and disposal. The solids are rinsed with a dilute citric acid solution (Flow 22) and water (Flow 23) before the are removed from the filter. Flow 29 is the solids rinses fed to an evaporator, where excess water is removed in Flows 14 and 15 to a receiver tank. Flow 26 is water from the evaporator receiver tank used to make up new citric acid solution or for rinsing collected solids. Flow 16 is the bottoms from the evaporator returned to the reaction vessel.

Water is produced in the destruction of most organic compounds. The water collected in the overhead receiver is this product water. Although most of the HCl in the product vapors will have been removed by the reflux condenser, it is expected that some HCl will be in the collected product water. Flow 24 is caustic solution to a neutralization tank to neutralize the acid content of the distillate. The neutralized distillate can then be fed to the evaporator (Flow 13) to return non-product water to the reaction vessel, or it can be taken directly to the evaporator overhead receiver (Flow 27) and from there to water treatment by Flows 17 and 19.

Materials of Construction

The 1000. L reaction vessel is specified to be tantalum-lined titanium. This construction provides excellent corrosion resistance (6) plus a strong and corrosion resistant pressure shell. The tantalum liner is expected to last the estimated 10. year lifetime of the unit, but even should it be breached the titanium shell will provide effective double containment until the process solution can be cooled and removed so that the liner can be replaced or repaired. A potentiometer connected between an electrically isolated counterelectrode in the process solution and the pressure shell will be able to detect any breach in the tantalum liner.

Other areas where the process solution will contact materials are in the solution cooler, filter, evaporator, evaporator bottoms pump, and evaporator bottoms return line. The solution cooler will be tantalum on the process side. Once the process solution has been cooled, it is compatible with Grade 7 titanium, which will be the material of construction for the solution filter, surge tank, evaporator, and associated plumbing.

Due to the HCl content of the hot gases exiting the reaction vessel, the reflux condenser and the overhead condenser will have process sides of tantalum. Once the gases have been cooled, Teflon-lined carbon steel will be used for the vent gas and condensate.

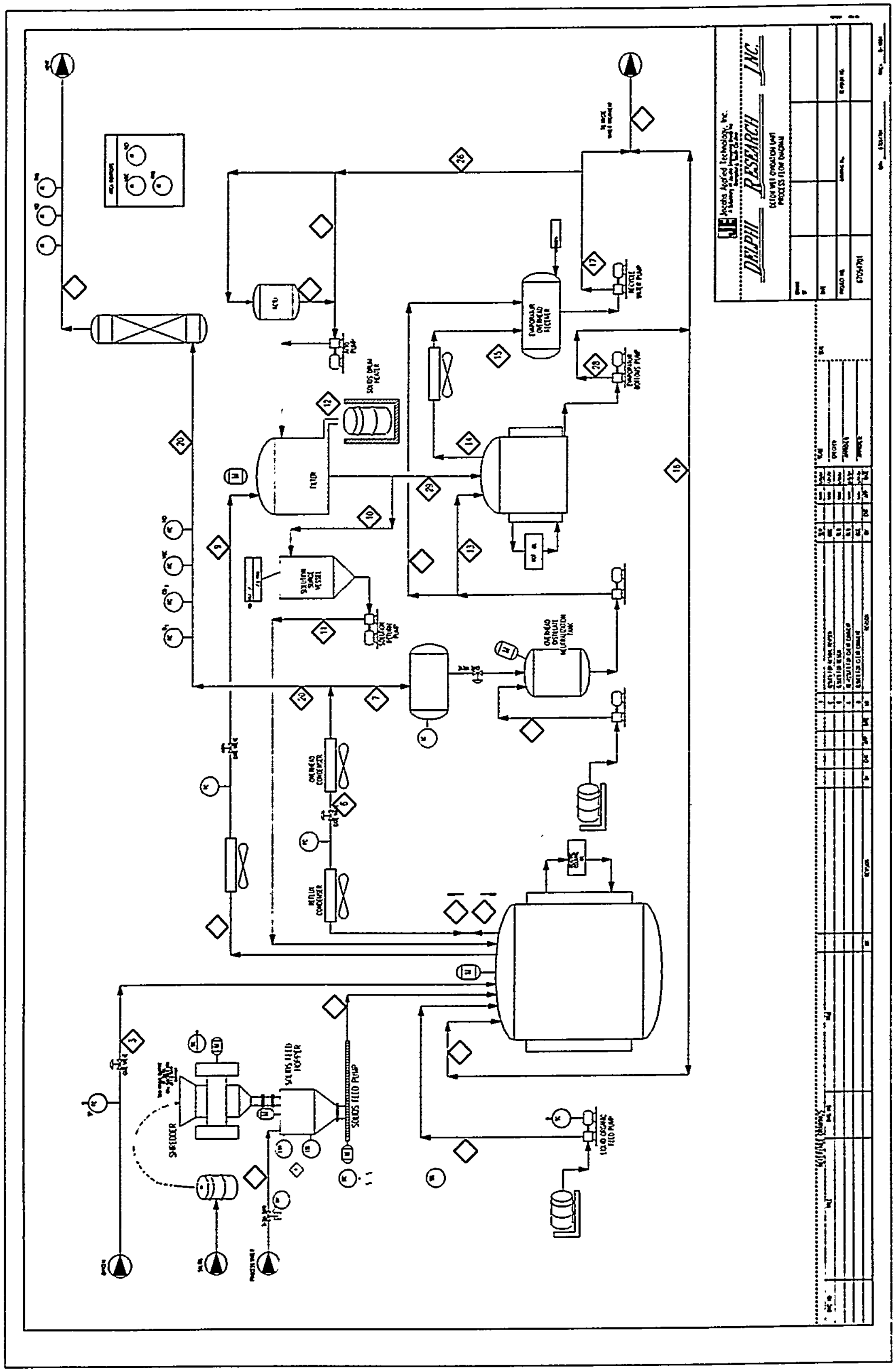


Fig. 2: Demonstration Unit PFD

Design Issues

Reliably feeding solid materials to the pressurized reaction vessel is a challenge. Solids will be shredded and slurried with water, then fed to the reaction vessel through redundant pinch valves using a progressive cavity slurry pump. Shredding will also increase reaction rate by increasing the surface area of the solids.

Effective agitation is vital to achieving good organic destruction rates, since the oxidation rate for most organic compounds is dependent on the surface area of contact between the organic compound and the process solution. Achieving effective agitation in the demonstration unit's reaction vessel is complicated by the range of waste forms. More volatile materials will be in vapor form, which will require good gas/liquid contact. Less volatile materials will be in liquid or solid form. Effective oxidation of liquids and solids will require good liquid/liquid and solid/liquid contact. In consultation with agitator companies, one of the more versatile arrangements was determined to be the combination of a standard 45.° pitched blade turbine mounted somewhat below solution level to pull vapor from the headspace of the reaction vessel into the process solution, and a disk/paddle turbine near the bottom of the reaction vessel to provide high shear. Baffles in the vessel will help provide good turbulence.

The combination of organic compounds and oxygen presents the potential for formation of explosive mixtures in the reaction vessel headspace. Computer simulations, conducted at Sandia National Laboratories (SNL), have indicated that below approximately 10.% by volume oxygen content in the reaction vessel headspace gases there is no flammability possible regardless of organic concentration. This is illustrated in Figure 3, which is presented here as a generic figure only and is not meant to represent actual data. Design parameters for the process specify operation at 5.% by volume oxygen in the vent gases, which translates to less than 1.% by volume oxygen in the reaction vessel headspace gases at operating conditions in the reaction vessel. These operational parameters give a large safe operating range (approximately 10x) for the process. Redundant, calibrated oxygen sensors on the vent gas line will ensure correct measurement of oxygen levels. Additional tests are planned at SNL to identify the flammability limits for some representative volatile organic compounds at the operating conditions of the process.

Place Figure 3 Here

An important issue in the unit's ability to destroy TBP was the ability of the filter system to remove ferric phosphate precipitate from the process solution at a rate sufficient to allow operation at the unit's design capacity of 25. kg/hr. Results of laboratory particle size measurements and filtration/rinsing experiments using ferric phosphate precipitated under the conditions of the process were used to size the filter. A sealed, Nutsche type or helical filter with a scraper/agitator will be used, so that filter cake rinsing and discharge will not normally require handling of the solids by the unit operators.

A preliminary layout of the equipment is shown in Figure 4. The demonstration unit is to be assembled as two transportable process modules plus a module for the oil cooling/heating system (not shown). A vertical module approximately 9.75 m tall x 3.66 m x 2.44 m will include the solids feed, reaction vessel, reflux condenser, solution cooler, particulate filter, surge tank, process solution return pump, evaporator and evaporator overhead condenser, evaporator bottoms return pump, and reaction vessel quench tank. A horizontal module approximately 7.32 m long x 2.44 m x 3.66 m high will include the remainder of the pumps, the overhead condenser, overhead receiver, evaporator overhead receiver, distillate neutralization tank, vent knock out tank, and vent gas carbon bed. A third module 7.32 m long x 2.44 m x 3.66 m high will contain

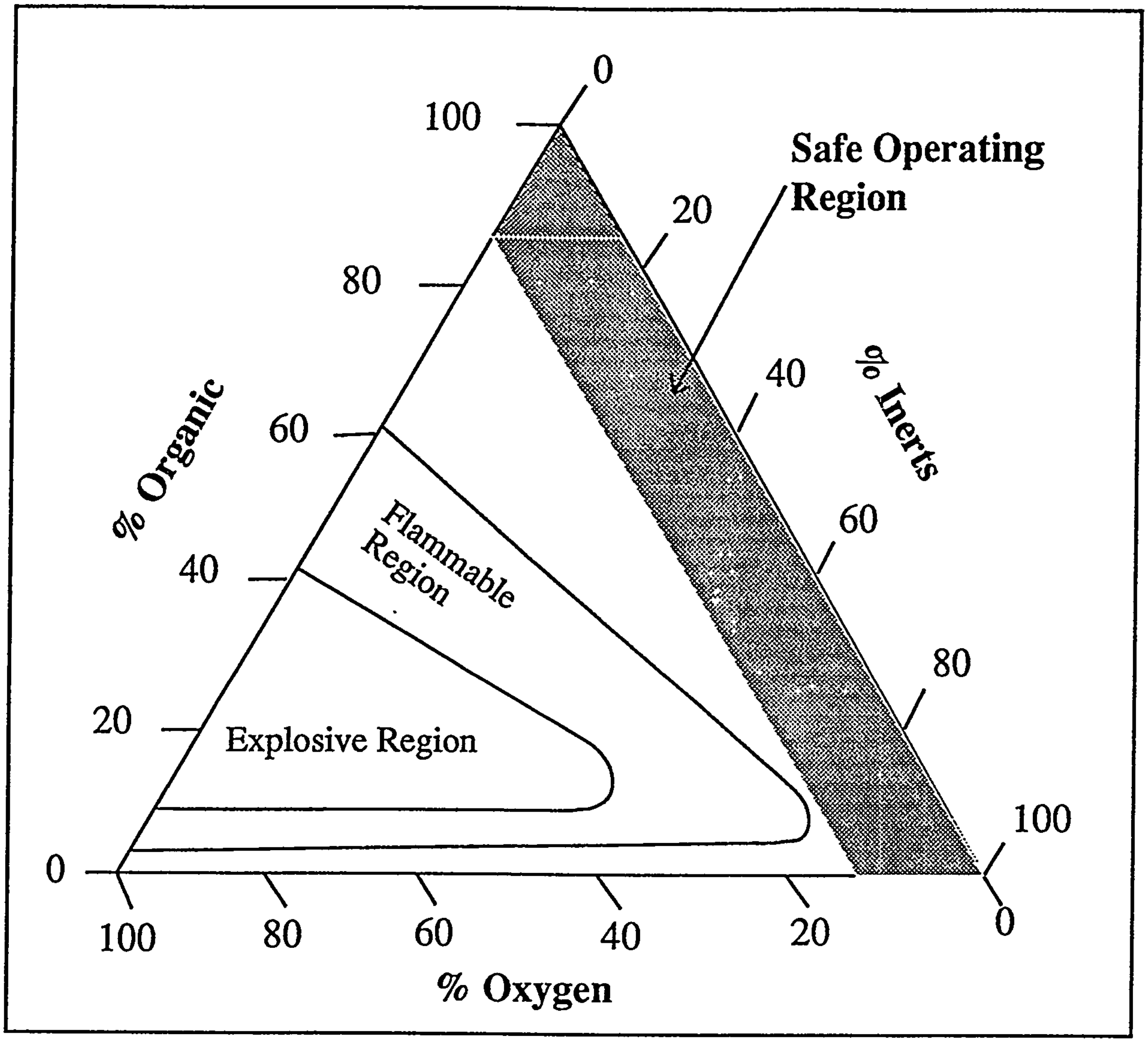


Fig. 3: Generic Flammability Curve

the oil cooling/heating system. The oil module can be placed away from the process modules and must in any case be placed in an exterior location so that excess process heat may be rejected.

Place Figure 4 Here

Fabrication and assembly of the demonstration unit is scheduled for fiscal year 1995.

DEMONSTRATION PLAN

The demonstration plan is a progression from tests with minimally hazardous or non-hazardous organic materials through treatment of hazardous organic wastes, and finally to demonstration of the process on a variety of mixed wastes. Non-hazardous and hazardous waste treatment is planned at SRS. Mixed waste treatment is planned at WSSRAP. The demonstration effort is planned to take place in Fiscal Years 1996 and 1997. A successful demonstration will establish the DETOX^{SM} process as a versatile, mobile on site mixed waste treatment method.

Non-Hazardous Materials Testing

After installation of the unit at SRS, functionality tests will be conducted to determine the ability of the unit to operate as designed, to identify any obvious flaws in control algorithms, equipment, materials, or construction, and to run through safety and emergency response procedures. Functionality tests will follow a progression from operation with cold water to operation with hot water and finally to operation with the process solution.

Following functionality testing the filter system will be tested for its ability to remove inert solids from the process solution, the solids feed will be tested separately for its ability to reliably deliver solids slurry to a pressurized environment, and the unit will be used to destroy a selection of minimally- or non-hazardous organic materials.

The liquid organic materials to be oxidized will be white petroleum oil and tributyl phosphate. The solids to be used in the solids feed will be a mixture of polyethylene, paper, latex rubber, and poly(vinyl chloride). The process vent gas, condensate, and solution will be monitored and analyzed to determine the levels of any volatile organics and to establish destruction efficiencies. After these tests, the unit will be inspected thoroughly to determine equipment compatibility and performance.

Hazardous Waste Treatment

Hazardous wastes to be treated include contaminated oils, non-halogenated solvents, halogenated solvents, and, if time and funding permit, combustible solids. The test regimen will most likely include benzene, trichloroethylene, tetraphenyl borate in water solution, and mineral oils contaminated with lead and/or mercury.

Vented product gas will be monitored for levels of volatile organic compounds, and the condensate product and process solution will be sampled and analyzed for organic residues to determine destruction efficiencies. When wastes containing toxic metals are destroyed, the process solution will be analyzed for the metals as well.

At the conclusion of hazardous waste treatment, the process solution will be boiled to evaporate HCl until approximately 95.% of the iron is in the form of the hydrated iron oxide. The iron oxide, which may contain toxic metals, will be filtered from the solution as it forms, and may be stabilized if SRS desires. The HCl will be condensed with the boiled water, neutralized with caustic, and disposed.

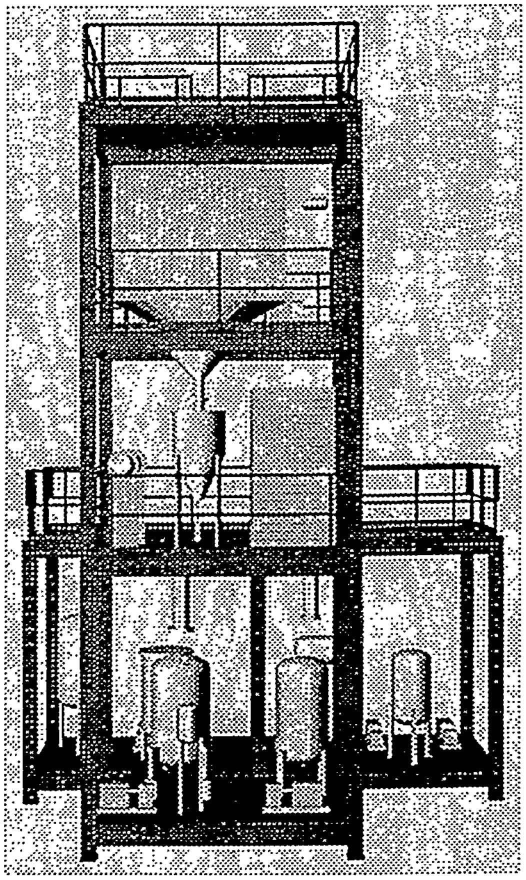


Fig. 4: Demonstration Unit Module Design

Following the hazardous waste campaign, the demonstration unit will be cleaned, thoroughly inspected, maintained, and any desired changes in design made before it is shipped to WSSRAP.

Mixed Waste Treatment

Mixed wastes to be treated include ethylene glycol, oils, non-halogenated solvents, halogenated solvents, paints and sludges, PCBs and PCB-contaminated liquids, and tributyl phosphate. The demonstration may be extended to other materials including combustible solids.

The unit will be installed, checked out, and an Operational Readiness Review conducted before mixed waste treatment is begun. The order of waste treatment will be as given above.

Calculations indicate that at least two process solutions will have to be used over the course of waste treatment to ensure that radioactivity is kept at low levels in the process solution residue. Vented product gas will be monitored for volatile organic compounds and radioactivity. Product water will be analyzed for volatile organic content and radioactivity, then sent to the on-site water treatment plant. The process solution will be analyzed periodically for organic compounds, radionuclide content, and toxic metals. The process solution residue and the ferric phosphate residue from treatment of tributyl phosphate will be stabilized and disposed at WSSRAP.

Demonstration Requirements

Requirements for the demonstration tests include: operating, safety, and maintenance manuals for the demonstration unit; formal test plans and procedures; hazardous materials handling and emergency response training for operators; lock out/tag out procedures; site-specific safety and operations training; NEPA documentation; a RCRA Part B R&D permit for tests with hazardous wastes at SRS; review of estimated water and air emissions by the cognizant regulatory agencies; and preparation of Radcon procedures, Safe Work Plans, and Task-Specific Safety Assessments for operations at WSSRAP.

ACKNOWLEDGMENTS

We gratefully acknowledge the support of the DOE Office of Technology Development (EM-50) and the DOE Morgantown Energy Technology Center in funding the development and demonstration of DETOX^{SM}.

REFERENCES

1. United States Patent Number 4,925,540, "Method for Treating Organic Waste Material and an Oxidation Catalyst/Cocatalyst Composition Useful Therefor", May 15, 1990.

2. United States Patent Number 5.047,224, "Method for Treating Organic Waste Material and an Oxidation Catalyst/Cocatalyst Composition Useful Therefor", September 10, 1991.

3. Bell, R.A. and P.M. Dhooge, 1994, "Design for Application of the DETOX^{SM} Wet Oxidation Process to Mixed Wastes", Proceedings of WM'94, the Symposium on Waste Management at Tucson Arizona, pp. 819-824, edited by Roy G. Post, The University of Arizona, Tucson, Arizona.

4. Moslander, J.E., D.T. Robertson, S.D. Goldblatt, R.A. Bell, and P.M. Dhooge, 1994, "Bench Scale Demonstration of DETOX^{SM} Wet Oxidation for Treatment of Hazardous, Radioactive,

and Mixed Wastes", Proceedings of the 1994 International Incineration Conference, pp. 451-455, University of California, Irvine, Office of Environment, Health, and Safety, Irvine, California.

5. Moslander, J.E., D.T. Robertson, S.D. Goldblatt, R.A. Bell, and P.M. Dhooge, 1994, "Bench Scale Demonstration and Conceptual Engineering for DETOX^{SM} Catalyzed Wet Oxidation", Proceedings of the International Topical Meeting on Nuclear and Hazardous Waste Management–Spectrum '94, pp. 72-77, American Nuclear Society, La Grange Park, Illinois.

6. Schussler, M. and C. Pokross, 1985, Corrosion Data Survey on Tantalum, Second Edition, Fansteel, Inc., North Chicago, Illinois.