Supercritical Water Oxidation Program (SCWOP)

Technology Summary

February 1994
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# SUPERCritical WATER OXIDATION PROGRAM

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The Department of Energy (DOE) established the Office of Technology Development (OTD) as an element of Environmental Restoration and Waste Management (EM) in November, 1989 (see Figure A). The organizational structure of EM-50 is shown in Figure B.

EM manages remediation of all DOE sites, as well as wastes from current operations. The goal of the EM program is to minimize risks to human health, safety and the environment, and to bring all DOE sites into compliance with Federal, state, and local regulations by 2019. EM-50 is charged with developing new technologies that are safer, faster, more effective and less expensive than current methods.

Figure A. DOE Organizational Structure as of June 1993.
In an effort to focus resources and address opportunities, EM-50 has developed Integrated Programs (IP) and Integrated Demonstrations (ID). In addition, EM-50 has developed special programs such as the Supercritical Water Oxidation Program to focus activities for addressing a very specific waste management or environmental problem.

An Integrated Program is the cost-effective mechanism used to solve a specific aspect of a waste management or environmental problem and can be either unique to a site or common to many sites. An Integrated Program supports applied research to develop innovative technologies in key application areas organized around specific activities required in each stage of the remediation process (e.g., characterization, treatment, and disposal).

An Integrated Demonstration is the cost-effective mechanism that assembles a group of related and synergistic technologies to evaluate their performance individually, or as a complete system, in correcting waste management and environmental problems from cradle to grave.

Figure B. Office of Technology Development Organizational Structure as of June 1993.
PURPOSE

The purpose of the Supercritical Water Oxidation Program (SCWOP) is to develop and demonstrate supercritical water oxidation (SCWO) as a viable technology for treating DOE hazardous and mixed wastes and to coordinate SCWO research, development, demonstration, testing, and evaluation (RDDT&E) activities with other Federal agencies, industry, and academia.

BACKGROUND

DOE has stored on its sites and facilities significant inventories of mixed waste, which fall under the Environmental Protection Agency's (EPA) Land Disposal Restrictions (LDRs). As such, this particular waste cannot be stored indefinitely, nor can it be disposed of without prior treatment to destroy, separate, or immobilize the hazardous component. The total volume of DOE mixed low-level waste in storage facilities has been estimated at nearly 589,000 m³*. In addition, DOE sites and facilities will generate significant volumes of mixed waste due to decontamination and decommissioning (D&D) activities and continue to generate significant quantities of mixed and hazardous waste as part of ongoing operations. Depending upon DOE's activities, as much as 60,000 m³ of mixed waste could be generated annually.

The Federal Facility Compliance Act (FFCA) of 1992 requires each facility that generates or stores mixed waste to prepare plans for treating all mixed wastes, or for cases where no treatment technology exists, to prepare plans for developing a treatment technology. The FFCA, which amends the Resources Conservation and Recovery Act (RCRA), provides the impetus for accelerated efforts to develop, design, and construct facilities that will render DOE mixed wastes into forms that can be disposed of legally and inexpensively.

SCWO technology holds promise for treating a portion of DOE's mixed waste. The process involves bringing together organic waste, water and an oxidant (such as air, oxygen, etc.) to temperatures and pressures above the critical point of water (374°C, 22.1 MPa). A schematic of a typical Supercritical Water Oxidation tubular reactor is displayed in Figure C. Under these conditions, the waste is treated at high organic destruction efficiencies of over 99.99% and the resulting effluents, which consist primarily of water and carbon dioxide, are relatively benign. In contrast to incineration, SCWO can easily be designed as a full containment process with no release to the atmosphere. In contrast to wet air oxidation, SCWO can achieve the high destruction efficiencies for hazardous wastes such as polychlorinated biphenyls (PCBs) or dioxins. In comparison to plasma treatment methods and even incineration, SCWO processes achieve high organic destruction efficiencies at much lower temperatures and without NOx production. In contrast to many thermal treatment technologies, SCWO can process wastes with low concentrations of organics.

For the past several years, DOE has undertaken a variety of SCWO RDDT&E initiatives in the areas of energy recovery and waste management. Recognizing this technology's potential for addressing DOE's mixed waste problem, DOE's Office of Technology Development established the SCWOP in the fourth quarter, FY92 to consolidate and focus the SCWO RDDT&E activities. The Idaho National Engineering Laboratory (INEL) is the lead laboratory for this program.

![Figure C. Typical Supercritical Water Oxidation tubular reactor process.](image)

**APPROACH**

SCWOP consists of a number of elements with the major element being the construction and demonstrations of hazardous and mixed waste pilot-scale (300-500 gallons per day throughput) SCWO units. Other elements include the reassessment and potential continuation and expansion of ongoing SCWO development activities across the DOE complex as well as those conducted by other research and development organizations. The program will also coordinate very closely with other Federal agencies, such as the Department of Defense, U.S. Navy, U.S. Air Force, U.S. Army, EPA, and Advanced Research Projects Agency.

The program will be conducted in two phases: Phase 1, the Hazardous Waste Pilot Plant (HWPP) Demonstration and Phase 2, the Mixed Waste Pilot Plant (MWPP) Demonstration. The goals of the HWPP Demonstration by 1996 are to:

- Demonstrate the technical viability and cost effectiveness of SCWO technology for treating DOE hazardous and surrogate mixed wastes; and
Provide sufficient design, operational, environmental, and safety data to evaluate the feasibility of a MWPP demonstration and to provide the design basis for the MWPP.

If a determination is made that the MWPP should be built and demonstrated, the goals of the MWPP Demonstration by 1998 are to:

- Demonstrate the technical viability and cost effectiveness of SCWO technology for treating DOE mixed wastes; and
- Provide sufficient design, operational, environmental, and safety data to evaluate the feasibility of a production-scale mixed waste plant and to provide the design basis for the production-scale plant.

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Supercritical Water Oxidation
Pilot Plant Demonstrations

Section 1.0
1.0 SUPERCRITICAL WATER OXIDATION PILOT PLANT DEMONSTRATIONS

TASK DESCRIPTION

The scope of work covered under this task is for the design, fabrication, permitting, operation, testing and evaluation of the HWPP and MWPP for treating DOE hazardous and mixed wastes. The HWPP demonstration will focus on identifying SCWO technology development needs, providing technology improvements required to demonstrate that SCWO is a safe, cost-effective technology, and demonstrating currently available SCWO technology using hazardous and surrogate mixed waste of interest to DOE. Data generated in the HWPP Demonstration will provide the basis for the decision of whether to proceed with the MWPP Demonstration and the design basis of the MWPP.

The MWPP will generate data to confirm the behavior of radionuclides during SCWO treatment, confirm the disposability of wastes from a SCWO unit treating mixed wastes, and demonstrate the shielding, additional control, and safety features required for a mixed waste facility. Data generated in the MWPP Demonstration will provide the basis for the decision of whether to proceed with a production-scale mixed waste treatment facility and the design basis of the production-scale facility.

In FY94, this task will focus on completing the HWPP design, selecting a site for the demonstration and obtaining the required permits. In addition, the conceptual design for the MWPP will be initiated to establish conceptual design parameters and develop estimates for cost and schedule.

TECHNOLOGY NEEDS

SCWO technology holds promise for treating a significant portion of DOE's mixed waste inventory. While this technology has been successfully demonstrated at the bench-scale and pilot-scale for a more limited number of wastes, numerous questions and risks remain in applying the process to DOE mixed wastes. To successfully design, construct, permit, and operate a mixed waste facility, data is required on scaling factors, materials technology and corrosion, thermodynamics and reaction kinetics for constituents of DOE wastes, operational hazards, performance of different process configuration, performance for the wide range in type and compositions of DOE mixed waste, chemistry and disposition behavior of radionuclides at SCWO conditions, and reliability and maintainability of the process for extended operating times.

The HWPP will provide much of this data without investing the substantial funds required to meet the requirements and regulations for a unit capable of treating mixed waste. Building on the data gained from the SCWO HWPP, the MWPP will be designed and will then be used to obtain the additional data required to evaluate, permit, design, and operate a full-scale facility that processes DOE mixed waste.

ACCOMPLISHMENTS

- Demonstrated proof-of-concept of a SCWO waste treatment unit;
- Developed an initial list of candidates wastes for SCWO treatment;
- Completed bench-scale testing using mixed waste surrogates;
- Completed specifications for the design of the HWPP, and
- Initiated HWPP design.

**COLLABORATION/TECHNOLOGY TRANSFER**

DOE will be working with the leading SCWO developers throughout the nation (i.e., other Federal agencies, national laboratories, universities, and private sector) to demonstrate SCWO technology for treating DOE hazardous and mixed wastes.

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Supercritical Water Oxidation
Technical Support

Section 2.0
2.0  SUPERCRITICAL WATER OXIDATION
TECHNICAL SUPPORT

TASK DESCRIPTION
The purpose of this task is to investigate and develop methods for mitigating corrosion and solids deposition at the various points in a SCWO system. The technical approach adopted involves conducting laboratory solubility measurements on important inorganic compounds in aqueous solutions at high temperatures. The water solubilities of candidate compounds for in situ neutralization of acids formed in a SCWO system will be measured over an appropriate range of temperatures. The results of these measurements will be used to upgrade the ASPEN Plus process model to include solubility and thermodynamic data for inorganic compounds under conditions relevant to the application of SCWO to DOE and commercial wastes. The reliability of the resulting upgraded process model in representing phase behavior for these substances will be demonstrated.

In FY94, laboratory measurements on additional classes of neutralizers and pilot studies on additional corrosion and deposition control strategies will be conducted. Results from laboratory measurements and other relevant data will be incorporated into the process-modeling (ASPEN Plus) software and experimental verification and testing of models will continue.

TECHNOLOGY NEEDS
This task addresses two significant problems which may limit the applicability of SCWO to a wide variety of aqueous waste streams, particularly those of interest to DOE. These two problems are corrosion of SCWO reactor components by acids and precipitation of solids. Solids precipitation may lead to problems either through production of solids, which remain behind in the SCWO reactor, or through the production of a relatively large volume of solids, which may become contaminated with radioactive elements present in the waste stream and hence, require disposal as solid low-level wastes. Acids are inherently formed in the SCWO process through oxidation of organic compounds containing heteroatoms (e.g., chlorine, phosphorous, sulfur) at high temperatures to produce the acids or oxyacids of these compounds. Metal ions present in the waste stream may also contribute to the overall acidity for formation of hydroxy species as a result of hydrolysis at high temperatures.

ACCOMPLISHMENTS
• Established a Cooperative Research and Development Agreement (CRADA) with the Modell Development Corporation (MODEC).
• Completed solubility measurements on the first set of candidate neutralizers.

COLLABORATION/TECHNOLOGY TRANSFER
The Oak Ridge National Laboratory has established a CRADA with MODEC to conduct cooperative research on the chemical issues relevant to SCWO.
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3.0 HOW TO GET INVOLVED

WORKING WITH THE DOE OFFICE OF ENVIRONMENTAL RESTORATION AND WASTE MANAGEMENT

DOE provides a range of programs and services to assist universities, industry, and other private-sector organizations and individuals interested in developing or applying environmental technologies. Working with DOE Operations Offices and management and operating contractors, EM uses conventional and innovative mechanisms to identify, integrate, develop, and adapt promising emerging technologies. These mechanisms include contracting and collaborative arrangements, procurement provisions, licensing of technology, consulting arrangements, reimbursable work for industry, and special consideration for small business.

Cooperative Research and Development Agreements (CRADAs)

EM will facilitate the development of subcontracts, R&D contracts, and cooperative agreements to work collaboratively with the private sector.

EM uses CRADAs as an incentive for collaborative R&D. CRADAs are agreements between a DOE R&D laboratory and any non-Federal source to conduct cooperative R&D that is consistent with the laboratory’s mission. The partner may provide funds, facilities, people, or other resources. DOE provides the CRADA partner access to facilities and expertise; however, no Federal funds are provided to external participants. Rights to inventions and other intellectual property are negotiated between the laboratory and participant, and certain data that are generated may be protected for up to 5 years.

Consortia will also be considered for situations where several companies will be combining their resources to address a common technical problem. Leveraging of funds to implement a consortium can offer a synergism to overall program effectiveness.

Procurement Mechanisms

DOE EM has developed an environmental management technology development acquisition policy and strategy that uses phased procurements to span the RDDT&E continuum from applied R&D concept feasibility through full-scale remediation. DOE EM phased procurements make provisions for unsolicited proposals, but formal solicitations are the preferred responses. The principle contractual mechanisms used by EM for industrial and academic response include Research Opportunity Announcements (ROAs) and Program R&D Announcements (PRDAs).
EM uses the ROA to solicit advanced research and technologies for a broad range of cleanup needs. The ROA supports applied research ranging from concept feasibility through full-scale demonstration. In addition, the ROA is open continuously for a full year following the date of issue and includes a partial procurement set aside for small businesses. Typically, ROAs are published annually in the Federal Register and the Commerce Business Daily, and multiple awards are made.

PRDAs are program announcements used to solicit a broad mix of R&D and DT&E proposals. Typically, a PRDA is used to solicit proposals for a wide-range of technical solutions to specific EM problem areas. PRDAs may be used to solicit proposals for contracts, grants, or cooperative agreements. Multiple awards, which may have dissimilar approaches or concepts, are generally made. Numerous PRDAs may be issued each year.

In addition to PRDAs and ROAs, EM uses financial assistance awards when the technology is developed for public purpose. Financial assistance awards are solicited through publication in the Federal Register. These announcements are called Program Rules. A Program Rule can either be a one-time solicitation or an open-ended, general solicitation with annual or more frequent announcements concerning specific funding availability and desired R&D agreements. The Program Rule can also be used to award both grants and cooperative agreements.

EM awards grants and cooperative agreements if fifty-one percent or more of the overall value of the effort is related to a public interest goal. Such goals include possible non-DOE or other Federal agency participation and use, advancement of present and future U.S. capabilities in domestic and international environmental cleanup markets, technology transfer, advancement of scientific knowledge, and education and training of individuals and business entities to advance U.S. remediation capabilities.

**Licensing of Technology**

DOE contractor-operated laboratories can license DOE/EM-developed technology and software to which they elect to take title. In other situations where DOE owns title to the resultant inventions, DOE's Office of General Counsel will do the licensing. Licensing activities are done within existing DOE intellectual property provisions.

**Technical Personnel Exchange Assignments**

Personnel exchanges provide opportunities for industrial and laboratory scientists to work together at various sites on environmental restoration and waste management technical problems of mutual interest. Industry is expected to contribute substantial cost-sharing for these personnel exchanges. To encourage such collaboration, the rights to any resulting patents go to the private sector company. These exchanges, which can last from 3 to 6 months, are opportunities for the laboratories and industry to better understand the differing operating cultures, and are an ideal mechanism for transferring technical skills and knowledge.
Consulting Arrangements

Laboratory scientists and engineers are available to consult in their areas of technical expertise. Most contractors operating laboratories have consulting provisions. Laboratory employees who wish to consult can sign non-disclosure agreements, and are encouraged to do so.

Reimbursable Work for Industry

DOE laboratories are available to perform work for industry, or other Federal agencies, as long as the work pertains to the mission of a respective laboratory and does not compete with the private sector.

The special technical capabilities and unique facilities at DOE laboratories are an incentive for the private sector to use DOE’s facilities and contractors expertise in this reimbursable work for industry mode. An advanced class patent waiver gives ownership of any inventions resulting from the research to the participating private sector company.

EM Small Business Technology Integration Program

The EM Small Business Technology Integration Program (SB-TIP) seeks the participation of small businesses in the EM RDDT&E programs. Through workshops and frequent communication, the EM SB-TIP provides information on opportunities for funding and collaborative efforts relative to advancing technologies for DOE environmental restoration and waste management applications.

EM SB-TIP has established a special EM procurement set aside for small firms (500 employees or less) to be used for applied research projects, through its ROA. The program also serves as the EM liaison to the DOE Small Business Innovation Research (SBIR) Program Office, and interfaces with other DOE small business offices, as well.

CONTACT

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**EM Central Point of Contact**

The EM Central Point of Contact is designed to provide ready access to prospective research and business opportunities in waste management, environmental restoration, and decontamination and decommissioning activities, as well as information on EM-50 IPs and IDs. The EM Central Point of Contact can identify links between industry technologies and program needs, and provides potential partners with a connection to an extensive complex-wide network of DOE Headquarters and field program contacts.

The EM Central Point of Contact is the best single source of information for private-sector technology developers looking to collaborate with EM scientists and engineers. It provides a real-time information referral service to expedite and monitor private-sector interaction with EM.

To reach the EM Central Point of Contact, call 1-800-845-2096 during normal business hours (Eastern time).

**Office of Research and Technology Applications**

Office of Research and Technology Applications (ORTAs) serve as technology transfer agents at the Federal laboratories, and provide an internal coordination in the laboratory for technology transfer and an external point of contact for industry and universities. To fulfill this dual purpose, ORTAs license patents and coordinate technology transfer activities for the laboratory’s scientific departments. They also facilitate one-on-one interactions between the laboratory’s scientific personnel and technology recipients, and provide information on laboratory technologies with potential applications in private industry for state and local governments.

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**For more information about these programs and services, please contact:**

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### ACRONYMS

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<th>Acronym</th>
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<td>Cooperative Research and Development Agreement</td>
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<td>D&amp;D</td>
<td>decontamination and decommissioning</td>
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<td>EM</td>
<td>Environmental Restoration and Waste Management</td>
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