

# SUPERCRITICAL WATER OXIDATION FOR TREATMENT OF MIXED WASTES

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## ABSTRACT

Supercritical water oxidation may be useful for destroying the hazardous components of mixed wastes, leaving the radionuclides for further processing. Technical issues related to various types of mixed wastes are discussed in this paper.

## INTRODUCTION

Supercritical water oxidation is an emerging technology that appears to have applications to the destruction of organic compounds and some inorganic compounds, such as cyanide and nitrate, in mixed wastes. The destruction of organic or other hazardous components in the mixed waste can allow the remaining radionuclides to be removed or treated by standard methods for remediating aqueous radionuclide waste streams.

Supercritical water oxidation takes place in a water medium with added oxidant at temperatures and pressures above the critical point of water (374°C and 22.13 MPa; Fig. 1). Under those conditions, water is a fluid with densities high enough that reasonably high process throughputs can be achieved in a vessel of a given size. Transport properties are gas-like. The solvent properties of supercritical water are different from those of liquid water, and as the waste mixture makes the transition, nonpolar compounds become soluble and salts become insoluble. An oxidant, such as air, O<sub>2</sub>, hydrogen peroxide, or another suitable compound must be present to achieve complete destruction of organic compounds and oxidizable inorganic compounds to CO<sub>2</sub>, water, and other innocuous compounds. Many hazardous organic wastes, including solvents, polychlorinated biphenyls (PCBs), and pharmaceutical wastes have been reported to be destroyed rapidly and completely in supercritical water.(1) These results should also be applicable to destruction of organic components of mixed wastes. In addition, certain characteristics of a supercritical water process might be utilized to achieve separation of radionuclides as a part of the process.

Although oxidation in supercritical water has superficial similarities to combustion, it apparently is sustained by a free radical chain reaction in the absence of a flame at a much lower temperature than incineration (about 400-700°C) and in a completely contained system. Almost no oxides of nitrogen are expected to be produced at these low temperatures.(2) All effluents can be completely controlled because the system is contained. In addition, because the critical point of water is at a higher temperature and pressure than the critical point of many organics, the mixture will be supercritical, and complete mixing is possible in a single-phase supercritical region. Thus, reaction

rates and destruction efficiencies are not limited by concentration gradients across phase boundaries, and reactions rapidly proceed to completion.

Because water is the reaction medium, the process can be used for a variety of aqueous wastes as well as non-aqueous wastes in dissolved or slurry form. An economic constraint on the oxidizable waste concentration arises from the amount of heat generated by its oxidation. The optimum concentration will vary with the heat of oxidation of the particular compounds present and the engineering design of the apparatus. An engineering tradeoff to be considered in the design of a plant is the waste concentration that generates enough heat to maintain the reaction, but not more than can readily be removed from the processing vessel. Pure or highly concentrated wastes can be diluted with water, whereas fuel or oxidizable wastes can be added to wastes present in low concentrations. Factors that influence the engineering design include the heat content of the fuel, the residence time in the reactor (determined by the chemical kinetics of oxidation of the waste), the physical state of the waste and its oxidation products, and the amounts of waste to be processed.

Supercritical water oxidation appears to be applicable to the destruction of most oxidizable components of mixed waste streams. Some of the many waste streams that might be treated by supercritical water oxidation include:

- liquid aqueous and organic streams at the point of origin, including machining wastes, paint wastes, automobile grease and lubricant wastes, PCB-contaminated oil, and waste solvents;
- stored wastes, including those that contain sludges or other solids; soil contaminated by spills or burial of organics;
- vermiculite and other mineral absorbers used to clean up spills;
- spent activated carbon; and
- wastes with particular hazards, such as mixed wastes or explosives.

The Los Alamos National Laboratory is investigating supercritical water oxidation for both the Department of Energy (DOE) Office of Technology Development and the Air Force Engineering and Services Center. In the DOE

program, the objectives are to obtain information necessary for evaluation of the technology and for process development, scaling up, and application to Department of Energy (DOE) wastes, including mixed wastes.(3) In this program, the kinetics of oxidation of model compounds in supercritical water have been investigated to determine the mechanisms of oxidation in supercritical water and to relate these mechanisms to those of gas-phase free-radical reactions. This work is being done for the purpose of developing correlations for scale-up and evaluation of the process. An integrated experimental system at a scale of 1 gal/hr is being used to investigate process variables and to develop data for scale-up.

The objective of the Air Force program is to determine the feasibility of destruction of propellant components in supercritical water. Open burning and open detonation of propellants and their wastes are becoming environmentally unacceptable, and alternative destruction technologies are needed. In the Air Force program, several propellant components, including ammonium perchlorate (AP), trinitrotoluene (TNT), and unsymmetrical dimethylhydrazine (UDMH) are being investigated for safe introduction into the supercritical water environment and the products of their destruction in supercritical water.

Many wastes produced by the DOE are mixed wastes. Some DOE mixed wastes are similar to industrial wastes, with the exception that a metal component of the waste is radioactive. An example of such wastes would be the machining fluids from plutonium and uranium machining, which may contain various organic solvents with traces of plutonium or uranium. Other DOE mixed wastes are unique to DOE operations; examples are the wastes from nuclear reprocessing generated at Hanford and Savannah River or radionuclide-contaminated explosives at the Pantex Plant. The various types of mixed wastes will present different technical issues for the application of supercritical water oxidation as a destruction method for the oxidizable components. These issues will be discussed in this paper in the context of results from the DOE and Air Force programs. Relevant data from the literature will also be presented.

#### DOE MIXED WASTES AND ASSOCIATED TECHNICAL ISSUES

At its present state of development, supercritical water oxidation is most readily applicable to liquid wastes. This technology can be expected to destroy organics and some inorganics, such as nitrate and cyanide, in mixtures with radionuclides. Metal radionuclide species will be present in output streams, as ionic species in the water, as solids, or a few metals may form volatile compounds. Thus, supercritical water oxidation is a method for treating mixed wastes to remove the hazardous component so that radio-

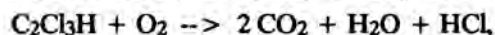
nuclides can be treated in subsequent steps. Technical issues associated with several types of mixed wastes are discussed below. This discussion is intended to be indicative rather than exhaustive.

#### Liquid Mixed Wastes

Early applications of supercritical water oxidation may be to liquid wastes with low solids content and that will produce low levels of solids. Examples of such wastes include machining fluids containing low levels of chlorinated compounds, hydrocarbon-tributyl phosphate mixtures and hexone from nuclear fuel reprocessing, and specialized processing wastes such as benzene from the tetraphenylborate separation of cesium, to be produced at Savannah River. These wastes can be expected to produce relatively low amounts of solids, and should not pose exceptionally difficult materials requirements.

#### Liquid Mixed Wastes Containing Solids and/or Producing Solid Precipitates

Mixed wastes containing solids, halogenated compounds, including machining fluids, solvents, and PCBs, and other wastes that can produce solids as they are oxidized, such as high concentrations of tributyl phosphate, will require provision for solids handling and will present additional issues of erosion and corrosion in the system. For example, in the case of chlorinated compounds, each formula-mole of chlorine in the waste will produce one formula-mole of HCl. It may be desirable to neutralize the HCl with NaOH or other caustics in the input stream. In this case, one formula-mole of NaCl will be produced for each formula-mole of chlorine in the waste. A large amount of salt can be produced from multiply halogenated compounds. For example, for every kilogram of the common solvent trichloroethylene (TCE) destroyed by the reaction



1.3 kilograms of sodium chloride would be produced with neutralization.

Salts are much less soluble in supercritical water than in liquid water, but this solubility depends to some extent on process conditions and appears to vary greatly with the particular salt. Solubility data for many salts are not available. Thus, the reactor, preheaters, and associated tubing and valves must be designed to prevent accumulation of solids that might cause plugging. A system must also be provided for removal of brine or salts from the system. Formation of solids in pressure let-down valves can cause plugging, while passage of solids formed before a let-down valve can cause erosion of valve components and tubing. Chloride and fluoride appear to be corrosive in the supercritical regime, as they are in liquid water, and may require specialized materials of construction. Phosphates and sul-

fates may deposit within the system unless process variables can be controlled to prevent deposition.

### Nitrate-Containing Wastes

Many mixed wastes produced by DOE facilities contain inorganic nitrates, because processes have been designed to take advantage of the favorable properties of actinide nitrates for processing and separation. Supercritical water oxidation may provide destruction of nitrate as well as other components of these wastes, including organics and ferrocyanides, thereby reducing the volumes of waste significantly and improving their qualities for further processing, including recovery of selected radionuclides, glassification, or grouting. Nitrate-containing wastes may be expected to be less corrosive than halogen-containing wastes, but evaluation of materials for heated sections will be necessary. Wastes containing high loading of solids may need to be preprocessed into a slurry or solution.

Although many salts are less soluble in supercritical water than in liquid water, mono- and divalent metal nitrates have been reported to remain in solution in concentrations up to 9.4 molal for  $\text{LiNO}_3$  at temperatures to  $450^\circ\text{C}$  and pressures to 30 MPa.(4) The phase diagrams for metal nitrate-water systems have not been determined, but it should be noted that the critical points for these mixtures are probably above these temperatures. Thus, these systems remain liquid under these pressures and temperatures. Even if nitrates are relatively soluble under supercritical water oxidation conditions, flow regimes and chemical reaction will need to be evaluated with consideration of prevention of solids formation. Deposition of several types of solids were observed in the processing of a simulated Hanford complexant concentrate waste.(5)

A further technical issue relating to nitrate-containing wastes is the chemistry of nitrogen-containing species under supercritical water conditions, in particular, the use of the nitrate ion as the oxidizing agent and the form of nitrogen-containing products. Thermodynamic calculations indicate that nitrate should be capable of oxidizing substrates of interest under supercritical water conditions and that higher nitrogen oxides should not be produced. However, the formation of nitrogen oxides by other thermal processes such as incineration and combustion in automotive engines is more critically affected by kinetics than by thermodynamics. Thus, experimental investigation of the behavior of nitrogen compounds under these conditions is necessary. The primary nitrogen-containing product observed under wet air oxidation conditions (below the temperature and pressure of water's critical point) is ammonia.(6) If salts are produced, their removal will be necessary as discussed above.

### Solid Mixed Wastes

Solid mixed wastes raise several technical issues: pretreatment for introduction into the processing unit, concentration limits, and processing unit design. The basis for solids introduction into a pressurized vessel has been laid by earlier work in coal processing and pressurized fluidized bed technology. Introduction of solids or slurries into the supercritical water oxidation system might be through lockhoppers. Such wastes as paper wipes, booties, and plastic containers may require maceration, shredding, pulping, or other specialized preparation for introduction into a supercritical water oxidation processor. Several approaches to reactor design are possible, including a fixed bed of the waste through which the oxidizing supercritical medium passes.

### Tritium and $^{14}\text{C}$

Mixed wastes containing tritium and  $^{14}\text{C}$  present special issues. Tritiated water can be expected to be a product of supercritical water oxidation of mixed wastes containing tritium. This tritiated water will be mixed and diluted with the process water, but all water will be contained in the processing system. Because all effluents are fully controllable, all effluents can be retained and further processed if necessary. For example, it may be possible to capture product  $^{14}\text{CO}_2$  as an insoluble metal carbonate.(7) Whether the end product is acceptable will depend on the nature of the waste, relevant regulations, and the availability of alternative and supplemental processing methods.

### General Issues for Mixed Wastes

Technical issues relating to all applications of supercritical water oxidation to mixed wastes will involve containment of radioactivity; operability, maintainability, and reliability of the overall system; safety of pressurized oxidation systems within hot cells or other containment facilities; and the nature of the output and its level of radioactivity. Radionuclides present in mixed wastes may undergo oxidation during transit through a waste processing unit. As a result, the compounds formed (probably oxides or hydroxides) may become insoluble in water. This can be desirable in achieving separations or concentration, but in any case, these transformations must be controlled for an acceptable product. Acceptability will depend on the additional processing necessary to stabilize the radionuclides. In addition, destruction of some of the components of the waste may result in a higher level of radioactivity in the effluent from the waste destruction unit. A supercritical water oxidation waste destruction unit used for mixed waste processing may produce solids, liquids, and gases containing radionuclides. In addition, some of the radionuclides, particularly those forming solids, may accumulate in the waste destruction unit. Control of all effluents to appropriate radiological

standards will be necessary, and eventual decontamination or disposal of the unit must be considered.

Safety dictates that all pressurized components of a supercritical water waste destruction system be properly certified, and double-contained as necessary for operation with radioactive materials. In many cases, this will mean operation within a hot cell, and remotely controlled equipment, with appropriate data acquisition functions, will be essential. If a waste stream varies in its characteristics, the use of artificial intelligence for process control may be important, to allow operation within all regulatory and engineered parameters. The presence of pressurized oxygen or other oxidizers such as hydrogen peroxide within a hot cell may also require special safety considerations. If plutonium or enriched uranium is to be processed, configurations leading to criticality must be avoided.

### SUMMARY

Supercritical water oxidation appears to be a promising technology for destruction of hazardous components of mixed wastes, allowing further processing for remediation of radionuclides contained in the wastes. Special considerations exist for processing of mixed wastes containing tritium and  $^{14}\text{C}$ . Normal safety and process design considerations for handling of radionuclides will apply to supercritical water oxidation. In addition, materials compatibility and solids handling techniques will require development for treatment of many mixed wastes. For mixed wastes containing nitrate, it may be possible to use the nitrate itself as an oxidizing agent, thereby bringing the cost of the process down and further reducing the total amount of waste.

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