



Project Summary

Supercritical Water Oxidation Model Development for Selected EPA Priority Pollutants

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The research summarized here involves the use of supercritical water oxidation (SCWO) technology as a method to destroy hazardous organic wastes. Kinetic models and reaction pathways for selected EPA priority pollutants were developed. Critical engineering issues were evaluated. These results were used to develop SCWO process strategy, improve reactor designs, and optimize operating conditions.

This Project Summary was developed by EPA's National Risk Management Research Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

The goals of this project were to assess the performance of SCWO in treating selected EPA priority pollutants and to enhance the development of SCWO processes. The project was executed in three phases. The first phase (year one) involved batch SCWO studies of five model compounds: acetic acid, 2,4-dichlorophenol (2,4-DCP), pentachlorophenol, pyridine, and 2,4-dichlorophenoxyacetic acid methyl ester (2,4-D methyl ester). The second phase (year two) consisted of detailed, continuous-flow tests involving both kinetic and mechanistic studies of 2,4-DCP and pyridine. The third phase (years one and

two) dealt with the evaluation of critical engineering issues such as corrosion and chromium speciation.

The task of pollution control has moved well beyond conventional technology. The present and future challenges of reducing toxic organic waste and sludge volume have overwhelmed existing waste management concepts. Based on 1984 estimates, extrapolated to 1990, hazardous wastes produced by industry range from 280 to 395 million metric tons/yr. Industries and municipalities continue to produce large amounts of biological sludges that must be dewatered, destroyed by burning, or disposed of by land farming. In addition, the federal government has large quantities of stored munitions and other organic wastes that must be treated. Listed among the military items requiring demilitarization are 340,000 tons of stored munitions. In addition, 30,000 tons of munitions are created each year. Presently, detonation and incineration costs are about \$800/ton and \$3,000/ton, respectively. Innovative and economical approaches must be found to manage existing contaminants and future stockpiles of unacceptable wastes.

Today, two of the national goals for hazardous waste management are: (a) greater than 99.99% destruction efficiency; and (b) treatment systems that are "Totally Enclosed Treatment Facilities." The supercritical water oxidation process can accomplish these objectives. The concept offers unique, economical, and innovative

solutions. By recovering heat from the effluent using heat exchangers, the SCWO process can become thermally self-sustaining, with wastes having a chemical oxidation demand of about 30 g/L or higher.

Since the early 1980s, a number of universities and companies have investigated the treatment of hazardous wastes in supercritical water. Early emphasis was on demonstrating the SCWO treatment concept and establishing treatability characteristics. During the last few years, however, it has become apparent that both fundamental and technical aspects of process design and commercial-scale development need to be addressed. In particular, design models for special wastes need to be developed.

Experiments and Observations

Experimental apparatus, test conditions, key observations, and data evaluation for batch and continuous-flow studies, as well as engineering evaluation, are summarized below.

Batch Study

Batch experiments were carried out at three temperatures (400°C, 450°C, 500°C), a constant water density (0.3 g/mL), and reaction times varying from 2 min to 20 min. The reactors were made of Stainless Steel 316 tubing (0.85 cm I.D. and 1.27 cm O.D.). The effective volume of a U-shaped reactor was 20 mL. Heat was provided by a fluidized sand bath. While in the sand bath, each reactor was mechanically vibrated to enhance mixing and heat transfer. Feed concentrations ranged from 40 mg/L to 3000 mg/L. Oxygen was used as the oxidant. The model compounds were analyzed by chromatographic techniques. Significant results were noted as follows:

- Destruction efficiencies of >99.99% were observed for pentachlorophenol at a temperature of 500°C and a reaction time of 2 min.
- Destruction efficiencies of >99% were observed for 2,4-DCP and 2,4-D methyl ester at a temperature of 500°C and a reaction time of 10 min.
- Acetic acid and pyridine, when compared with the chlorinated aromatics, were relatively refractory, but destruction efficiencies >99% were observed at a temperature of 500°C and a reaction time of 20 min.

- Qualitatively, as determined by GC analyses, SCWO of 2,4-DCP and 2,4-D methyl ester produced noticeable amounts of intermediate compounds (about 20) at either lower temperatures (< 450°C) or shorter reaction times (< 5 min), and the number of these intermediates reduced to about three when the temperature and reaction times were > 450°C and > 5 min.
- SCWO of acetic acid, 2,4-DCP, and pyridine followed pseudo-first-order reaction kinetics. Activation energies for acetic acid, 2,4-DCP, and pyridine, respectively, were 106, 28.5, and 91.5 kJ/mole.
- Pyridine and 2,4-DCP were recommended for more detailed kinetic and mechanistic studies involving continuous-flow SCWO reactor systems.

Continuous-Flow Study

The continuous-flow experiments were conducted using a plug-flow reactor setup. One reactor was made of Stainless Steel 316 tubing (0.635 cm O.D. and 0.165 cm wall thickness). A second reactor was made of coiled Hastelloy C-276 tubing. The feed flow rate was 35 g/min. The tests were performed at temperatures varying from 400° to 520°C, residence times ranging from 2 sec to 11 sec, >200% excess oxygen, and a pressure of 27.6 MPa. The Reynolds number ranged from 7400 to 8200. Feed concentrations varied from 300 mg/L to 800 mg/L for 2,4-DCP and from 1000 mg/L to 3000 mg/L for pyridine. The major findings are summarized as follows:

- More than 10% of the 2,4-DCP was hydrolyzed by supercritical water at temperatures above 450°C. The rate of hydrolysis was first-order with respect to the concentration of 2,4-DCP. The activation energy and preexponential factor were 209 kJ/mole and $10^{12.2} \text{ sec}^{-1}$, respectively.
- The overall oxidation and hydrolysis reaction rate (r) for 2,4-DCP was found to be $r = A \exp(-E_a/RT) [2,4\text{-DCP}][\text{O}_2]^{0.35}$, where the activation energy (E_a) and preexponential factor (A) were 88.9 kJ/mole and $10^{5.5} \text{ sec}^{-1}(\text{mole/L})^{-0.35}$, respectively.
- Nine intermediate compounds were identified during the SCWO of 2,4-DCP: 2-chlorophenol, 4-chlorophenol, 2,6-dichlorophenol, phenol, chloride,

acetic acid, formic acid, carbon dioxide, and carbon monoxide. Based on these compounds, a simplified reaction pathway for the SCWO of 2,4-DCP was developed.

- Less than 5% of the pyridine was hydrolyzed by supercritical water at the highest tested temperature, 522°C. Therefore, the SCWO rate was approximated by the overall oxidation and hydrolysis reaction rates. The SCWO rate for pyridine was found to be $r = A \exp(-E_a/RT) [\text{Pyridine}][\text{O}_2]^{0.2}$, where E_a and A were 210 kJ/mole and $10^{13.1} \text{ sec}^{-1}(\text{mole/L})^{-0.2}$, respectively.
- Seventeen intermediate compounds were found in the effluent derived from the SCWO of pyridine. These compounds included carboxylic acids, dicarboxylic acids, amines, ammonia, carbon dioxide, and carbon monoxide. Based on these compounds, a simplified reaction pathway for the SCWO of pyridine was developed.

Engineering Evaluation

Material Performance

Three nickel alloys (Stainless Steel 316, Hastelloy C-276, and Monel 400) were evaluated. The experiments were conducted using a batch reactor setup at three temperatures (300°C, 400°C, and 500°C), three pH conditions (2.1, 5.8, and 8.6), varying water densities (0.09 g/cc to 0.3 g/cc), fixed oxygen loading (2.1 MPa), constant chloride concentration (420 mg/L), and uniform coupon exposure time (100 hr). The following observations were made:

- Both localized (pitting and crevice) corrosion and uniform corrosion were apparent in all three alloys under the test conditions, and additionally, selective leaching of the Monel 400 alloy was observed at supercritical water temperatures ranging from 400°C to 500°C.
- For both Stainless Steel 316 and Hastelloy C-276 and a given pH, higher corrosion rates were observed at test temperatures of 300°C and 500°C as compared to 400°C.
- Generally, the lowest pH condition (2.1) created the most severe corrosion.
- For Stainless Steel 316, the least corrosion, 0.03 mils per year (mpy), occurred at a temperature of 400°C and pH of 5.8, and the worst corrosion,

1.89 mpy, corresponded to a temperature of 300°C and pH of 2.1.

- For Hastelloy C-276, the least corrosion, 0.06 mpy, occurred at a temperature of 400°C and pH of 5.8, and the worst corrosion, 1.33 mpy, corresponded to a temperature of 500°C and pH of 5.8.
- Among the three alloys, Monel 400 displayed the most corrosion under the test conditions.

Chromium Speciation

Generally, in an SCWO process, chromium it can be introduced from the influent or it can result from corrosion of the reactor system. Since some alloys currently used for SCWO studies contain high chromium contents, the concentration of chromium species in reactor effluents could reach a unacceptable level.

The chromium speciation study was conducted with the use of a vertical, concentric-tube reactor. The reactor was made of Stainless Steel 316 which contained 16 wt% chromium. Tests were conducted at varying temperatures (300°C to 450°C), feed flow rates (45 g/min to 120 g/min), and a fixed pressure (25 MPa). Chromium concentrations of the influent and effluent were monitored. Both municipal and industrial sludges were used. The following observations were made:

- The speciation of chromium, trivalent or hexavalent, showed direct correlation with the effluent pH. When the effluent pH was less than 7, trivalent chromium was the only detectable chromium species, and when the effluent pH was greater than 7, both trivalent and hexavalent chromium corrosion products were produced.
- The level of hexavalent chromium in the treated effluent decreased more

than 10 times, 0.046 mg/L to 0.004 mg/L, when the process temperature changed from 300°C to 400°C (pH 7.9).

- At 400°C, the concentration of precipitated hexavalent chromium at the reactor bottom (0.288 mg/L) was much higher than the effluent hexavalent chromium concentration (0.004 mg/L), whereas at 300°C, the hexavalent chromium concentration at the reactor bottom (0.035 mg/L) was comparable to the effluent hexavalent chromium concentration (0.046 mg/L).
- The concentrations of trivalent chromium in the treated effluents decreased only 50%, 0.39 mg/L to 0.16 mg/L, when the process temperatures changed from 300°C to 400°C.
- The precipitation of hexavalent chromium was due to a substantial decrease in solubility of chromic and chromate salts in supercritical water. Chromium separation by precipitation was affected by temperature, specific co-ions, and co-ion concentration.
- Soluble trivalent chromium was retained in the mass that settled in the reactor bottom. Co-precipitation with insoluble and associated soluble salts appeared to be the mechanism by which the trivalent chromium was removed.

Conclusions and Recommendations

- Refractory and chlorinated organic compounds, such as acetic acid, 2,4-DCP, pentachlorophenol, pyridine, and 2,4-D methyl ester, were effectively destroyed by the SCWO process.
- These five model compounds exhibited a wide range of reactivity in SCWO environments, indicating the

effect of chemical and structural features of each compound on the overall reaction rate.

- Kinetic models were developed for 2,4-DCP, pyridine, and acetic acid.
- Mechanistic studies involving 2,4-DCP and pyridine provided an insight into the possible reaction pathways and by-product transformation.
- The breakdown of complex organic molecules under SCWO conditions produced a large number of unstable compounds and a small number of relatively stable, lower-molecular weight, intermediate compounds.
- By adjusting the reaction conditions, the type and amount of intermediates produced can be controlled, resulting in more efficient reactor design and higher destruction efficiency.
- For a given temperature, the highest corrosion rate occurred at the lowest pH in the test conditions, which ranged from pH = 2.1 to pH = 8.6. For a given pH, higher corrosion rates were observed at 300°C and 500°C than at 400°C.
- The relative formation of chromium species (trivalent and hexavalent) can be controlled by adjusting the pH of the reaction media.
- Chromium species, hexavalent in particular, can be precipitated effectively because of the limited solubility of chromate salts in supercritical water.

The full report was submitted in fulfillment of Cooperative Agreement No. CR-816760-02-0 by the Separations Research Program, Center for Energy Studies, and Environmental and Water Resources Engineering, Department of Civil Engineering, The University of Texas at Austin, under the sponsorship of the U.S. Environmental Protection Agency.

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The complete report, entitled "Supercritical Water Oxidation Model Development for Selected EPA Priority Pollutants," (Order No. PB95-230975; Cost: \$17.50 subject to change) will be available only from:

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