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DESTRUCTION OF TOXIC ORGANIC MATERIALS USING SUPER-CRITICAL WATER OXIDATION: CURRENT STATE OF THE TECHNOLOGY

R. W. SHAW
US Army Research Office
Research Triangle Park, NC 27709-2211
USA

N. DAHMEN [1]
Forschungszentrum Karlsruhe
Karlsruhe D-76021, Germany

1. Introduction

In 1966 John Connolly of Standard Oil Co. published remarkable data on hydrocarbon solubilities in water at high temperatures and pressures [2]: he observed that, in some regions of the phase diagram, hydrocarbons (e.g., benzene, heptane) and water are miscible in all proportions. Rapid development of experimental techniques made Connolly's work possible and speculations began about the consequences of his observations. For example, in 1970 Gerhard Schneider suggested the extension of wet air oxidation to higher temperatures for disposal of organic materials [3]. In the mid 1970's Sanjay Amin, a student working with Robert Reid and Michael Modell at Massachusetts Institute of Technology (MIT), studied decomposition of organic compounds in hot water and found that the intractable tars that formed below the critical temperature of water, disappeared above it. Research and development on supercritical water oxidation (SCWO) for disposal of organic waste materials began soon after [4].

This paper reviews a specific application of the properties of high temperature water; the properties themselves are discussed in depth elsewhere in these proceedings. We emphasize, however, that understanding of the SCWO process brought by basic research is crucial to successful development and application of the technology. The foremost contributors to our understanding of high temperature water and its solutions are E. Ulrich Franck and his collaborators at Karlsruhe. In particular, their photographs of luminous hydrocarbon/ oxygen flames at supercritical conditions brought considerable attention to these remarkable processes [5].

As a medium for chemical reactions, depending on its density, supercritical water has both gas-like and liquid-like properties. The gas-like low viscosity promotes mass transfer. The liquid-like density promotes solvation. The low dielectric constant promotes dissolution of non-polar organic materials. The high temperatures (for water, $T_c = 374^\circ\text{C}$) increase thermal reaction rates. These properties provide a reactor medium in which mixing is fast, organic materials dissolve well and react quickly with oxygen, and salts precipitate.

The SCWO reactor is enclosed and under control: the system is not in contact with the outside and it can be quickly shut down. The operating temperatures are much lower than a typical incinerator, so nitrogen oxides are not formed. SCWO systems can be made compact and portable: they can be taken to the toxic waste site. In spite of these advantages, development and acceptance of SCWO has been slow. This paper discusses technical and other reasons for this slow progress and outlines some current developments of SCWO reactors including the prospect for its use in destroying chemical weapons. One of us (RWS) has been involved in the US Army program to develop SCWO and that program is emphasized. Technical details have mostly come from universities and national laboratories. Information on SCWO development from industry has been limited by concerns about proprietary information.

For comparison, we show three oxidative waste treatment processes:

Wet Air Oxidation (Zimpro, 30 y old, 100's in use):

- 150 - 300 °C, 10 - 200 bar
- 3 phases - solid, liquid, gas
- residence time: 10 - 100 min

Supercritical Water Oxidation (SCWO):

- 500 - 650 °C, 200 - 1000 bar
- 1 phase - supercritical fluid
- residence times: 10 sec - 1 min

Incineration (oldest oxidation technology known):

- 800-1100 °C, 1 bar
- 3 phases - solid, liquid, gas
- residence times: (o) sec

Oxidation in hot water, either below or above the critical temperature, is often called “hydrothermal oxidation” or HTO. This term reduces the chance of misunderstandings by people who are not scientists (e.g., that “critical” refers to a nuclear critical mass) and emphasizes the large region of the pressure/temperature phase diagram in which wastes can be treated. We have listed some of the advantages of SCWO, but all technologies have their strengths and weaknesses and the choice of waste treatment process should depend on a broad range of factors: technical, economic, etc.

2. Origins of SCWO

General Atomics (GA) licensed technology from the early work at MIT for gasification of organic materials in SCW and, in the early 1980's, began developing and patenting methods for oxidation of organic compounds in supercritical water. Patents by GA since 1982 include reactor designs, solids handling, effluent quenching, reaction rate enhancers, heat transfer, and corrosion resistant materials. The first contract with GA for a major reactor system was awarded in 1992 by the Defense Advanced Research Products Agency and the Office of Naval Research. Subsequently GA designed and built several other reactors and gathered considerable data on reactor materials and behavior of a range of wastes in SCWO.

During the 1980's Michael Modell designed and built SCWO reactors at the companies MODAR and MODEC and reported on destruction of organic compounds including polychlorinated biphenyls and DDT to >99.99% efficiency without formation of dioxins [6]. Subsequent development led primarily to use of the cylindrical tank at MODAR and the tube at MODEC. In 1989, one of us (RWS) saw demonstrations at MODEC of the treatment of municipal sewage sludge and of paper mill waste. These malodorous, viscous materials went in one end of the reactor and odorless products came out: clear water, gases, and, for the sewage sludge, a fine powder of iron oxide and aluminosilicates – soil present in the original feed material.

Stimulated by the work of Modell and his colleagues, Cheryl Rofer at the Los Alamos National Lab began exploring the potential of SCWO for treatment of wastes for the US Department of Energy in 1986. In 1987, collaborating with Jeff Tester and his group at MIT, they began studies of reaction kinetics of simple molecules in SCW. Subsequently, the US Air Force began supporting SCWO for disposal of explosives. The Los Alamos program expanded significantly and, in 1991, Steven Buelow began as director. The team at Los Alamos has focused on treatment of explosives and radioactive mixed waste. Their comprehensive program has been characterized by work ranging from basic research to reactor design and testing and close collaboration with universities and industry.

Richard D. Smith and his group had been working on supercritical fluid chromatography and materials processing at the Pacific Northwest Lab and organized a workshop, “Supercritical Fluid Technologies: Basic Research Needs [7] in 1987 for the Army Research Office and Office of Naval Research. At that workshop, James Welch of NIST-Boulder reported on his design and tests of a tank reactor for the disposal of contaminated torpedo fuel and Modell spoke on SCWO. Among the research recommendations from that workshop report are: “Both the synthesis and destruction of materials in chemical reactors are important applications of the novel properties of supercritical fluids...studies of phosphonates in supercritical fluid solvents could give insight into the destruction of various nerve agents”. Recommendations from that workshop had a major influence on the subsequent SCWO program in the DOD: for example, a proposal by ARO for a system to destroy chemical weapon

agents led to the 1992 US Defense Advanced Research Projects Agency and Office of Naval Research contract with General Atomics. In 1998 the US Army chose SCWO as part of the process to destroy nerve gas stored at Newport, IN.

Stimulated in part by the workshop just described, Sheridan Johnston of Sandia-Livermore Lab visited laboratories working on SCWO. In Karlsruhe, he saw the luminous flames in water discovered by Franck's group. Soon Sandia began a research program and in 1989 tested a MODEC reactor with nuclear weapon waste simulants. Sandia exploited their spectroscopy expertise, built flow reactors with optical access, and, in 1990, they produced supercritical water flames. In 1991, Steven Rice and his colleagues at Sandia did feasibility tests for the Army on the destruction of smokes and dyes – polyaromatic compounds including salts. During this period, their program was supported by a military environmental protection fund [8]. The project continued with collaboration from Jeff Tester's group at MIT who measured reaction kinetics of organic compounds.

The Sandia program included studies of reactor materials, modeling and experiments on hydrothermal flames, experiments on the treatment of propellants and explosives and radioactive "mixed" waste, experiments and modeling of hydrothermal flames, and high-pressure thermodynamics modeling. Quantum chemical calculations by Carl Melius [9] indicated that coordination with water molecules by organic molecules undergoing reactions would significantly reduce activation energy barriers and accelerate reaction kinetics.

Ernest Gloyna began research and engineering of SCWO at University of Texas-Austin in 1988. Among the subjects of this comprehensive program [10] were reaction kinetics, salt formation, mass and heat transfer, catalysis, and corrosion. Gloyna and his colleagues explored a range of reactor types and contributed to the development of the Eco-Waste Technologies commercial system.

In 1990 the US Army Research Office organized the NATO Advanced Research Workshop, "Destruction of Toxic Molecules in Supercritical Water". This workshop developed specific recommendations for research to provide fundamental understanding of the chemistry of hazardous materials in SCWO. Understanding the processes enables rational design of reactors, setting of optimum operation parameters, prediction of reactor materials lifetimes, and anticipation of reactor upsets. Some of the participants summarized that NATO workshop in an article for the American Chemical Society that brought the basic concepts of supercritical water as a reaction medium to a wide audience [11].

From 1992 – 1998, the US Army "Chemical Reactors" program was active at Massachusetts Institute of Technology, University of Delaware, and University of Texas-Austin. This cooperative multi-investigator program was based on the research plan developed in the 1990 NATO workshop and sought to provide fundamental understanding of all aspects of treatment by SCWO of nerve and mustard agents and explosives and propellants. More than sixteen university professors [12], scores of students, and their collaborators from Los Alamos, Sandia, and NIST studied reaction kinetics and mechanisms, reactive intermediate species, ion association, properties of solutions, nucleation and deposition of salts, electrochemistry and corrosion, and reactor modeling.

3. Reactor Designs and Operating Conditions

Reactor designs fall into three groups: tubular (pipe), tank, and transpiring wall. Tubular flow reactors are, to our knowledge, most common. Tank reactors may be used when salts are present – the heavy brine (not in the supercritical phase) remains on the bottom of the tank from which it may be drawn off. Transpiring walls allow clean water to enter through apertures in the cylindrical reactor wall - the clean transpiration water maintains a boundary layer free of corrosive species or depositing solids on the inner reactor surface. The concept of transpiring wall technology was borrowed from the gas turbine industry.

Clearly, if a salt brine is present, the reactor is not operating on a single phase. In these systems, the chemistry appears to occur in the supercritical phase above the condensed brine. In tubular flow reactors, very high pressures may be used to keep salts in solution; but, depending on the solubility of components in the feed stock, tubular reactors also may not be strictly single-phase systems.

The SCWO reactor environment is hostile: hot water that may, depending on the feed material, contain chemically active ions. Reactors are made of metal alloys that resist corrosion and tolerate high temperatures. The high nickel Hastelloy and Inconel alloys have high temperature stress-rupture strength and creep resistance and are resistant to corrosion and oxidation. Stainless steel 316, which has substantial chromium and nickel and is relatively corrosion and creep resistant, has been used for SCWO reactors operating under milder conditions. Even these high performance alloys may not withstand the most challenging oxidation mixtures and liners (e.g., Ti) that are used.

Because the dielectric constant of water depends on the temperature, ion activity changes as the temperature of the reaction mixture changes. Experience has shown that corrosion is most serious in the heat-up or cool-down sections of the reactor where the temperatures are high, but not so high to cause ion association and reduce chemical activity.

During their development of SCWO for chemical weapon agents, General Atomics performed corrosion tests on materials including nickel alloys, reactive metal alloys (e.g., Ti and its alloys), refractory metals (Mo, Nb, Ta), noble metals and their alloys (Pt, Rh, Ir), and ceramics [13]. The heteroatoms in chemical agents (P, S, and halogens) lead to acid environments that must be neutralized leading, in turn, to the formation of salts. Exposure to strong acids over a range of high temperatures simulating heat-up and cool-down indicated that Pt and Ti were most resistant, but that the reactor material should be matched to the waste material. Nicolaos Boukis et al. from the Karlsruhe Forschungszentrum have studied corrosion of metals in high temperature water in the presence of acids and oxygen [14]. Ronald Latanision and his group from MIT have studied corrosion in SCWO and have developed an understanding of material stability using exposure studies and molecular simulations [15], [16].

A group of experts met in 1995 to identify data needed to support modeling of SCWO reactors for toxic material destruction; their recommendations include studies in chemical kinetics, physical transport and mixing, thermodynamics, thermochemistry, and phase separations [17]. CFD Research Corp. with OLI Systems, Inc. and the MIT Energy Lab are working together to model SCWO oxidation reactors. They have coupled advanced thermodynamic and kinetic models for SCWO with a general-purpose computational fluid dynamics code. Having developed models for methane and methanol and validated them with experimental data, these investigators are now extending their codes to multi-component waste mixtures and salt formation [18].

4. Current SCWO Technology in the United States

4.1 LOS ALAMOS NATIONAL LABORATORY

Two principal reactor systems are now in development at Los Alamos. A down-flow reactor for actinide contaminated wastes (ion exchange resins, paper and plastic lab trash) is 1 inch in diameter and 14 inches long. Residence time for waste in the reactor is 30 seconds. The reactor is made of A286 stainless steel with a Ti liner (clean water is run outside the liner). After pyrolysis to transform the waste into pumpable fluid, SCWO occurs at 46 MPa and 540 °C

A tubular 500-foot long vertical coil reactor will be used for disposal of explosives including nitramines and nitrocellulose. The reactor is made of Inconel 625. After hydrolysis of the explosive in NaOH, SCWO is performed at 110 MPa (high pressure to enhance salt solubility) and 450 °C. The very high pressure enhances the solubility of the high concentration of salt from the hydrolysis step. The waste residence time in the reactor is several minutes and the measured half-life for destruction is a few seconds, so the destruction efficiency is very high.

4.2 TYNDALL AIR FORCE BASE

The Air Force plans to award contracts to build SCWO systems for a broad range of organic wastes at their depots. A tubular reactor built by GA will soon start up for testing. These systems will handle up to two gallons/min of feed (waste + water). The Air Force also seeks systems (with SCWO as one element) for waste disposal at foreign bases. Wastes come from medical and aircraft maintenance activities, gray water (wash and laundry), and sewage. The Air Force program is based on work by GA, Eco Waste Technologies, Inc., University of Texas-Austin, and Thiocol.

4.3 US ARMY

During the autumn of 1998, a SCWO reactor will be tested for destruction of colored smokes and dyes – polyaromatic compounds including salts. Previous bench scale testing of a transpiring wall reactor at Sandia-Livermore Lab indicated successful operation without plugging by salts. Approximately 10⁴ tons of smoke and dye compounds require disposal at the Pine Bluff Arsenal in Arkansas. The reactor was built by a consortium led by Foster Wheeler Corp, Gencorp Aerojet designed and built the transpiring wall reactor, and Sandia-Livermore provided basic research and technical support. High concentrations of Na and Ca salts drove the reactor design

decision. The reactor is designed to run 24 h/day and treat 10 gm/sec of waste at 600 °C and a residence time of 10 sec. Acid produced during treatment of the waste is neutralized by strong base. Oxygen gas is the oxidant.

The Army has called for proposals for a large SCWO system to serve as the second stage of a plant to destroy the nerve gas, VX, stored at Newport, IN. After treatment of the organophosphonate with strong base, the hydrolyzed product will undergo SCWO. Design of these plants requires attention to all aspects of a complex process of which SCWO is only a part. Responders to the Army's call are likely to be large engineering consortia with broad experience in chemical plant design and including a partner with SCWO reactor design skills.

4.4 US NAVY

As part of their "environmentally sound ships" program, the Navy has commissioned SCWO reactors for disposal of black water (sewage), gray water (sinks, showers), paint, solvents, contaminated fuel, oil, etc. The engineering requirements are challenging: the reactor throughput must exceed 40 g/sec of waste, they will be in intensive use (10 hr/day) and must occupy a space no larger than 8 ft x 9 ft x 10 ft. Two units are in test in 1998: a downflow tubular design by General Atomics and a transpiring wall by Foster Wheeler/Aerojet. Systems will be judged on their throughput and destruction efficiency, nature of their effluents, corrosion and plugging, safety, reliability, and consumables required.

4.5 COMMERCIAL SYSTEMS IN THE US

General Atomics has three pilot (or demonstration) systems now operable; all are vertical, down-flow reactors designed to operate at 650°C and 24 MPa. We refer to them as GA1, GA2, and GA3. The GA1 reactor (mentioned in Section 2) was developed for destruction of chemical weapon agents (nerve and mustard gas), propellants, and other military toxic materials. Destruction of chemical agents was demonstrated at Illinois Institute of Technology in a bench-scale system. GA1 has a Ti liner, an inside diameter of 4.3 in., wall thickness of 1.6 in., is 62 in. long, and has a capacity of 1 gal/min. Compressed air is the oxidant. The system has a modular design and is built on skids so that it can be transported. Its cumulative operation time is over 500 hours. GA reports that they can handle reaction mixtures with salts at 20 weight percent.

GA2 was built for the Air Force for destruction of rocket propellants. It is slightly smaller than GA1 and is lined with Ti. Capacity is 0.6 gal/min. This reactor has processed wastes with 6 weight percent of solids and has cumulative operation time of several hundred hours. In 1998, this system will be moved from Thiokol, a manufacturer of rocket motors, to the Army Dugway Proving Ground where it will be used for testing on chemical weapon agents and energetic materials. As part of an upgrade for these tests, the GA1 reactor will be relined with Pt, and adapted to the GA2 system.

GA3, the Navy shipboard reactor, is the largest GA reactor with an inside diameter of 7.25 in. and length of 59 in. and a capacity of 2 gal/min. The system fits within an 8 ft x 9 ft x 10 ft. volume, and is designed to destroy shipboard hazardous liquids. It is lined with Ti and has 200 hours operating time. In cooperation with Stone and Webster [19], GA is also developing shipboard SCWO effluent particle and heavy metal removal systems based on filtration and ion exchange. This program seeks to produce reactor liquid effluent that can be discharged directly into ocean waters.

In 1994, Eco Waste Technologies built and began operation of the first and (to our knowledge) only commercial SCWO reactor currently in routine operation in the US. This reactor, operated by Huntsman Corporation in Austin, Texas, treats a variety of long chain alcohols and amines at 5 gal/min. The effluent is suitable for discharge to normal water treatment plants and, according to the operators, produces total organic carbon less than 5 ppm and destruction efficiencies above 99.9999%. The tubular flow reactor operates at 26 MPa and temperatures from 540 – 650 °C. Eco Waste has been active in reactor development and holds numerous patents.

Eco Waste has several foreign associates: Shinko Pantek in Kobe, Japan has licensed Eco Waste technology to build a 5 gal/min sludge treatment plant. Chematur Eng AB in Karl Skoga, Sweden is building a 1-2 gal/min operating unit for organic laden waste waters and sludge.

MODAR developed a reactor to treat wastes from a pharmaceutical plant in 1986 and had a successful demonstration operating at 50 – 500 gal/day. A change in environmental regulations removed the need for this plant and, to our knowledge, it is not in operation. In 1995, MODAR was acquired by General Atomics.

5. Current SCWO Technology – Europe

Several groups in Europe are doing basic research and process development of SCWO for the treatment of wastes from production of pharmaceuticals, paper and chemicals. Since 1997, activities to some extent have been coordinated within the nationally funded EU COST working group D 10 [20]. This work explores the use of supercritical water and ammonia for chemical transformations and syntheses and supports chemical process developments already started by applied research. Most of the fundamental research will be done at the Universities of Nottingham, Loughborough, Darmstadt and at the Forschungszentrum Karlsruhe (FZK) and focuses on reactions of organic compounds in SCW (hydrolysis, hydration/dehydration, partial oxidation, and homogeneously catalyzed reactions) and new syntheses in SC ammonia. The applied research for the process development of SCWO will be done at the University of Helsinki and at the FZK Karlsruhe in cooperation with a pilot plant at CHEMATUR. Research for the gasification of biomass and organic waste in SCW will be done at the FZK in cooperation with SPQL International b.v. (Netherlands). The following outlines the principal SCWO activities in Europe [21].

5.1 GERMANY

Most of the European activity is in Germany. Eckhard Dinjus and his colleagues at FZK have a broad program on basic and applied SCWO [22] and on kinetics of oxidation in CO₂ and CO₂/water mixtures. Research on kinetics, corrosion [23] [24] and materials has been performed in a range of reactor designs:

- 1) a laboratory tube reactor (7 m , 2.1 mm id, 1 kg/h) for kinetic studies.
- 2) a tube reactor (15 kg/h , 600°C, 30 MPa, 15 m of 8 mm id, air as oxidant) has treated a variety of different waste from pharmaceutical, chemical and paper industry, and municipal wastes.
- 3) a film-cooled two-zone reactor (150 kg/h, 600°C, 30 MPa, 1 m of 56 mm id, air as oxidant). A porous stainless steel tube, through which the coolant flows, is inserted in a pressure resistant tube of a Ni-based alloy.
- 4) A floating-type reactor is used for the treatment of halogenated hydrocarbons [25]. Two vertical coaxial flows are established: a reactant central flow inside an alumina tube reactor and an inert flow outside the reactor tube but within a pressure-resistant tube of Inconel 625. Hydrogen peroxide is the oxidant. Heat is removed by a counter-current coaxial cooling stream of water in a horizontal cooling zone. The reaction mixture can be neutralized at the inlet of the cooler.
- 5) The Karlsruhe Institute has installed another co-axial reactor concept mainly for corrosion studies (0.7 m of 12 mm id, 600°C, 50 MPa, 0.3 kg/h). The space between the two tubes, an outer pressure vessel and an inner tube made from ceramic material, is connected via a movable gasket to prevent pressure differences [26].

The research group, “Supercritical Fluids”, of the Forschungsverbund Karlsruhe maintains a large basic research effort on kinetics, thermodynamics and modeling of physico-chemical properties, especially in fluid CO₂ and water. Collaborators include the Universities of Karlsruhe, Stuttgart and Darmstadt, the Fraunhofer Institute (ICT), and FZK; the principal investigators are Eckhard Dinjus, Ulrich Müller, Karlheinz Schaber, Horst Hippler, Bettina Kraushaar-Czarnetzki, Henning Bockhorn, Matthias Ballauff, and Herbert Vogel.

The Fraunhofer Institute ITC operates several batch and continuous reactors for the treatment of solid and liquid waste in a program led by Thomas Hirth:

- 1) a tube reactor (30 MPa, 600°C, 12 l/h) for liquid or suspended wastes including electronic scrap.
- 2) a mobile plant (35 MPa, 600°C, 20 l/h) for the treatment of hazardous liquid waste at the source of generation.
- 3) a pressure transducer for pulse-free feeding of gaseous or liquid flows at high conversion pressures up to 200 MPa (volume 0.5 l).
- 4) diverse batch reactors (32.5-200 MPa, 350-600°C, 0.03-2 l/h) for parametric studies.

Daimler Benz, Ulm in cooperation with the Fraunhofer Institute (ICT) are setting up a process for the treatment of electronic scrap [27]. Technical University Munich operated a bench-scale SCWO-plant of 50 kg/h for the treatment of waste that could not be destroyed by biological systems. In these experiments, various model compounds were treated with hydrogen peroxide. These activities were terminated in 1996 [28]. Technical University Hamburg Harburg developed the combined process of soil extraction [29] followed by SCWO with

electrolytic in-situ generation of oxygen. Soil was taken from a former paint factory, clay loam and other contaminated sites.

MODEC installed a pilot plant in cooperation with a consortium of pharmaceutical companies at the Fraunhofer Institute (ITC) [30]. The reactor (200 m, 550-600°C, 25 MPa, 90 l/h) used high flow rates to keep particles moving and prevent them from settling on the walls [31],[32]. This cooperation came to an end in 1996.

5.2 FRANCE, SWEDEN, SWITZERLAND, AND SPAIN

C.E.A. (Commissariat à l'Énergie Atomique), Pierelatte, is operating a 4 kg/h continuous tube reactor (400-600°C, 20-60 Mpa, 5-15% organic feed) to treat organic components of radioactive waste under the direction of Stephane Sarrade [33]. At 500°C and 30 MPa the nuclear fuel cycle solvent dodecane is fully oxidized into water and CO₂. Addition of phosphorous (TBP) or natural uranium in the simulated waste does not reduce the conversion rate of the organic content.

C.N.R.S. (Université Bordeaux, Comp. Europ. d'Etudes en Environment Industriel, François Cansell) investigated the destruction of model substances for de-inking sludge in a 3 kg/h continuous plant [34] and is about to install a pilot plant in cooperation with ELF-Aquitaine.

Chematur Engineering, AB, Karlskoga in January 1999 acquired the exclusive world wide rights to Eco Waste SCWO technologies. Already in early 1998 Chematur inaugurated its 250 kg/h SCWO demonstration facility based on the Eco Waste process under the trade name Aqua Critox³⁵. The successful tested wastes are waste water from amine production (1.5-2.0 wt.%), de-inking sludge and spent cutting liquids (amine containing) from metalworking, treated at 25 MPa up to 600°C with oxygen. The off gas of the amine containing effluents showed significant levels of N₂O of up to 25 % of the initial nitrogen content.

ETH Zürich developed the concept of a film-cooled coaxial hydrothermal reactor [36]. Two coaxial tubes form the reactor, waste water enters the central tube, and the oxidant enters the outer tube. The walls of the reactor are cooled by a water film of 80-250°C to retard precipitation of solids and corrosion of the pressure vessel. Hydrothermal flames, estimated at 1700-2200°C can be observed through windows. The plant was designed for 15 kg/h at 42 MPa and 600°C and was patented by Sulzer Chemtech AG 1995 in the USA [37].

Under the direction of M. Jose Cocero, the University of Valladolid operates a film-cooled SCWO reactor filled with Al₂O₃ balls for mixing and increasing conversion rates[38]. This reactor was used for the treatment of synthetic dyestuff wastewater. The reactor volume is 15 l (effective volume 9 l) with operating conditions of 25 MPa, 600-700°C, 12-17 kg/h mass flow, organic content of 7-11 wt.%, and air oxidant. The reactor is energetically self-sufficient with feed preheated by the energy recovered from the reactor.

6. Current SCWO Technology in Japan

The Organo Corp. acquired a license for MODAR technology through 1995. They have built a tank reactor to test treatment of municipal water and sludge, electronic wastes, and polychlorinated biphenyls.

Tohoku National Industrial Research Institute is studying poly-chlorinated bi-phenyls and waste polymers. Kumamoto University is studying sewage sludge treatment and University of Tokyo the kinetics of SCWO of phenol.

7. Technology Transfer of SCWO

SCWO may appear exotic, but the Zimpro process (operating at lower temperatures and pressures) has been in commercial use for 30 years. The major obstacles to development of SCWO applications have been: 1) lack of fundamental understanding, 2) corrosion of reactor materials by some feed stocks, 3) fouling of reactors by salts precipitating from some feed stocks.

Successful reactors have been built and operated based on experience and trial and error; but, except for a few compounds, we lack the fundamental understanding of reaction kinetics as a function of temperature and pressure that would enable rational reactor design. We emphasize again that fundamental understanding also enables setting of optimum operation parameters, prediction of reactor materials lifetimes, and anticipation of reactor upsets.

New technologies require an induction time before they are accepted. The time is considerably increased when one deals with hazardous materials, treatment of which requires a lengthy procedure of review and granting of permits. The US Army's choice of SCWO for disposal of nerve agent is an important step forward for the

technology. That choice came after years of expert evaluation and comparison of competing technologies by, among other groups, the US National Academy of Sciences [39].

We have mentioned the interest by companies outside the US in treatment of sewage sludge by SCWO. Within the US sludge is usually dried and spread on the land – a cheap disposal process. Where abundant space for spreading is not available, SCWO may be an economically viable alternative and may replace other currently used technologies such as incineration. Wastes from pharmaceutical and other biotechnology plants are especially suitable for SCWO.

The principal engineering challenge for SCWO reactor development is not the reactor itself, but preparation of materials for introduction into the reactor, pumping to bring the reaction medium up to pressure, and managing the let down of products back to ambient pressure. Economics for the SCWO process appear favorable: Modell has calculated that, with a heat exchanger to recover reaction heat, one can operate a reactor at 2% organic feed with no additional fuel [40]. Workers have also proposed to recover unused oxidant and to condense product CO₂.

8. Summary

The development of SCWO for disposal of organic materials is being explored around the world and has already been found useful in a broad range of applications. Over the past decade, our understanding of the fundamental chemistry of this complex process has increased markedly; but much remains to be learned and this area is wide-open for basic research on a fascinating medium for chemistry.

Treatment of organic materials with low concentrations of heteroatoms (e.g., sulfur, phosphorus, and halogens) is straightforward. SCWO is challenged by organic waste materials containing large concentrations of heteroatoms (e.g., nerve and mustard agents, and chlorinated hydrocarbons). The processing chemistry of these materials causes the production of corrosive acids. Neutralization of these acids forms salts that may be corrosive and may foul or plug the reactor. Corrosion is most serious in heat-up and cool-down sections of the reactor where the dielectric constant of water is higher and ion association is reduced. Corrosion and salt formation have been the principal obstacles to development of SCWO applications. Even for challenging wastes, however, reactor designs and materials of construction promise effective, economical waste treatment.

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