Hydrolysis and Oxidation in Subcritical and Supercritical Water: Connecting Process Engineering Science to Molecular Interactions

*J.W. Tester and J.A. Cline**

ABSTRACT

Key engineering issues influencing the development of supercritical water oxidation (SCWO) for waste treatment were reviewed. Major chemical pathways and kinetics for hydrolysis and oxidation reactions of model organic wastes were discussed. In selective examples, results from extensive laboratory-scale measurements were compared with molecular simulations of solvation and reaction effects in supercritical water. Connections between reaction chemistry and observed corrosion in SCWO processing equipment were discussed to underscore the importance of understanding electrochemical phenomena over a wide range of temperature and density conditions. Research needs for improved understanding of physical and chemical effects in supercritical fluids were identified.

KEY WORDS: hydrolysis, molecular interactions, oxidation, process engineering, supercritical water, waste treatment

BACKGROUND

General Information on Hydrothermal and Supercritical Water

Properties of Water in the Critical Region — Pure water has a critical point at 374°C and 221 bar. Near this critical point, water has a large heat capacity, typically 2 to 6 times that of liquid water and its isothermal compressibility is very large (≈ 0.04 bar^{-1}). In this region, the solvation properties of water also change dramatically — correlating directly with density changes that are sensitive to pressure and temperature.[1] For example, at 250 bar, sodium chloride (NaCl) is very soluble (37 wt%) at 25°C, but at 550°C, the solubility is only 120 ppm. Water's ability to shield charge diminishes as its dielectric constant decreases from 80 at ambient conditions to ≈ 2 at 250 bar and 400°C. Conversely, in the critical region, organic materials and noncondensible gases become soluble. For example, benzene (C_6H_6) at temperatures above 300°C and 250 bar is completely miscible in water over all concentrations. Gases such as oxygen (O_2), nitrogen (N_2), carbon dioxide (CO_2), and even methane (CH_4) are also completely soluble in supercritical water. With these solvation characteristics, supercritical water is an excellent medium to carry out oxidation of organics contained in aqueous waste streams.

Destruction Efficiency — Supercritical water oxidation (SCWO) systems are capable of providing high destruction efficiencies of organics with small residence times. Typical destruction and removal efficiencies (DRE) can exceed 99.999% for normal operating conditions of 250 bar, 600°C, and residence times of 60 s or less. These DRE levels meet requirements for destruction of Environmental Protection Agency (EPA)-controlled substances and United States Department of Defense (U.S. DOD) chemical weapons stocks. A SCWO system can be contained entirely, allowing products to be stored

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* Department of Chemical Engineering and Energy Laboratory, Massachusetts Institute of Technology (MIT), Cambridge, MA 02139.

[1] Although the supercritical solutions were concentrated in other components frequently resulting in properties that significantly deviated from the pure-water case, the use of the term "critical point" always refers to pure water conditions to provide a constant frame of reference.

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for analysis, if necessary. At normal operating conditions, hydrocarbons are converted to CO_2 and water. Although CO_2 is a greenhouse gas, it can be recovered at pressure and liquefied for reuse or sequestration. Heteroatoms such as phosphorus and sulfur are converted to phosphate and sulfate anions, which, depending on pH control, will remain as their respective acids, or if neutralized may precipitate out as salts (such as NaCl and sodium sulfate [Na_2SO_4] when sodium hydroxide [NaOH] is used). Nitrogen heteroatoms are abstracted to form primarily N_2, with trace amounts of nitrous oxide (N_2O), but not NO_x, which is formed under higher temperature conditions.

Applications of SCWO

EPA-Regulated Wastes — Dilute aqueous wastes containing organic residues can be treated effectively using SCWO to acceptable DRE levels for a wide range of toxic compounds, from low molecular weight solvents (such as methanol [CH_3OH], methylene chloride [CH_2Cl_2], and trichloroethylene [$C_2H_3Cl_3$]) to high molecular weight polycyclic aromatics (such as polychlorinated biphenyls [PCB]).

National Aeronautics and Space Administration (NASA) Human Waste Treatment — NASA has investigated SCWO for use in remediating biomass and human metabolic waste for long-term space flight. Because resources in space are scarce and payload material is finite, it becomes necessary for spacecraft personnel to treat and recycle cellulosic metabolic waste materials quickly and efficiently, which normally would be remediated on a longer time scale by the Earth’s ecosystem.

U.S. DOD Chemical Demilitarization — The United States’ chemical weapons stockpile has been targeted for destruction. To this end, various technologies for hazardous waste destruction are under evaluation for feasibility, reliability, and cost-effectiveness. Among these are SCWO, incineration, molten metal treatment, electrochemical oxidation, and flash photolysis. The chemical weapons stockpile presents a considerable challenge to SCWO in terms of operational logistics, as the chemical agents are transported frequently in nontoxic form, as “hydrolysate,” which represents a hydrolyzed form of the agent formed by reaction with NaOH. As this detoxification process increases the pH, this also changes the corrosion regime, and possibly could have a major impact on the treatment process selected.

U.S. Department of Energy (U.S. DOE) Mixed Waste Remediation — The U.S. DOE is considering SCWO as an option for removing the organic components of mixed, low-level radioactive wastes. As the inorganic components, which harbor the majority of the radioactivity, are sparingly soluble in supercritical water, the SCWO process lends itself naturally to separation of the radioactive inorganic components, while simultaneously mineralizing all organic components to CO_2, H_2O, and N_2, and acid products for any heteroatoms present (i.e., hydrochloric acid [HCl], sulfuric acid [H_2SO_4], and phosphoric acid [H_3PO_4]).

Commercial SCWO and Competing Technologies

SCWO recently has gone commercial. In 1994, EcoWaste Technologies successfully used SCWO to treat wastewater sludges. General Atomics acquired the MODAR[†] process and has demonstrated that it can be used for the destruction of U.S. DOD chemical weapons and solid rocket propellants.

While incineration is the chief competitor to SCWO, there are also other waste treatment technologies targeting the same market. These include catalytic oxidation, molten metal treatment, electrochemical oxidation, flash photolysis, and microbial degradation. SCWO is particularly well suited to dilute aqueous wastes (with total organic carbon [TOC] contents from 1 wt% to 20 wt%), which are too concentrated for absorptive (activated carbon) remediation and too dilute for effective incineration or molten metal reforming.

Limitations of SCWO

Just as SCWO is well suited for the rapid destruction of organic compounds, the thermal environment of sub- and supercritical water is generally too aggressive for organic synthesis reactions. While the idea of a tunable solvent, in terms of dielectric constant and density is attractive from the point of reaction kinetics optimization for rate and selectivity, the critical temperature for water is 374°C. As many organic compounds are oxidized readily or hydrolyzed at such temperatures, the scope of organic reactants where this is a viable synthesis medium is very limited. The high pressures needed also are a drawback in that pumping power requirements and system containment are important concerns for SCWO to meet operability and economic criteria as a waste treatment option.

OVERVIEW

Process Equipment and Flowsheets

A typical SCWO system begins with two or three feed streams — an oxidizer stream, an organic stream (the destruction target), and possibly an auxiliary fuel stream (Figure 1). These feed streams are brought up to pressure separately and preheated separately. Reactant streams are fed to the reactor, which may be a vessel or a continuously fed stirred-tank reactor (CSTR), or a tubular, plug-flow-type reactor (PFR).

[†] Trade name.

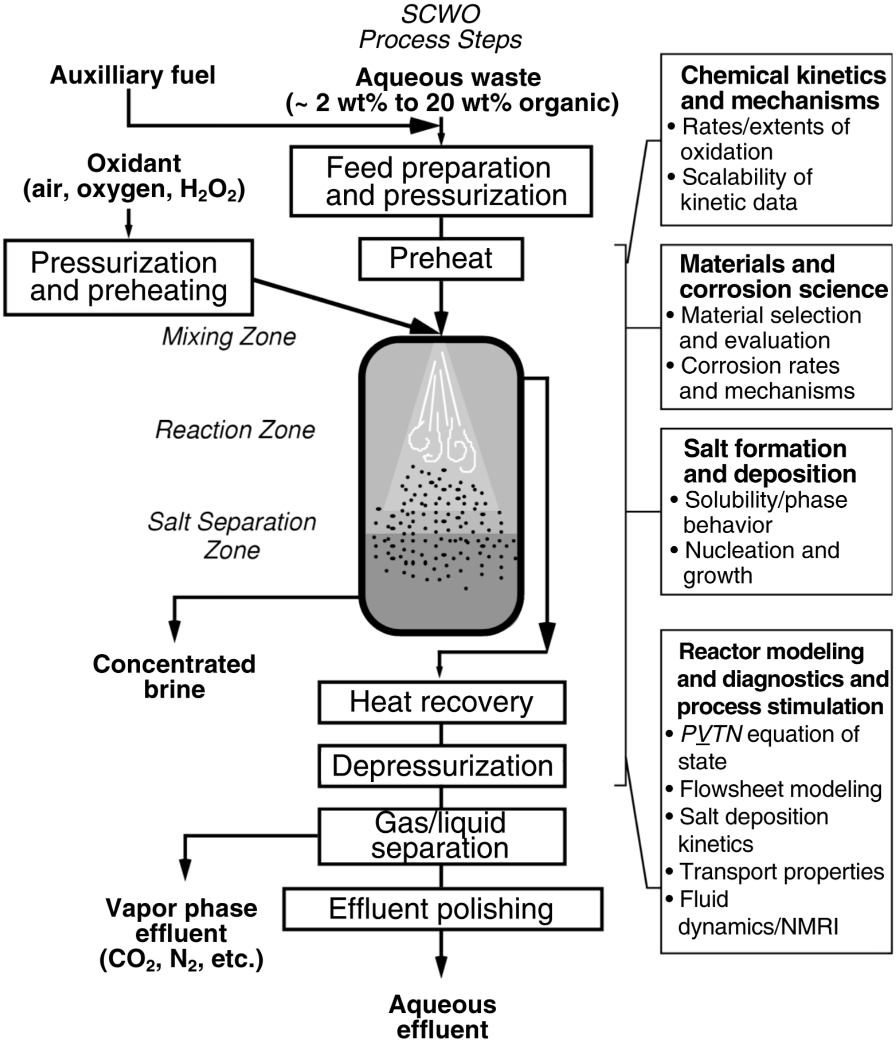

FIGURE 1. *General process flowsheet for SCWO showing major process steps and relevant areas of research.*

CSTR — The vessel and CSTR have prolate vertical aspect ratios and two major temperature zones, which are designed to facilitate solids handling and mitigate corrosion. The top zone is the hot reaction zone, operating isobarically at supercritical pressures with temperatures ranging from 400°C to 650°C. In this top zone, most of the oxidation takes place, producing mainly CO_2 and H_2O. Mixing actually is accomplished by the large differences in local fluid density, which depend strongly on temperature and concentration; the buoyancy forces create substantial convective transport rates. Depending upon the pH of the feed streams, heteroatoms such as P and S oxidize in the hot zone to PO_4^{3-} and SO_4^{2-}, can precipitate out as salts (Na_2SO_4), or persist as acids (H_2SO_4). Solid precipitates settle into the lower cooler zone, while lower density, fluid phase products are carried upward through an exhaust port. The lower zone is a cool zone, which contains a dense, brine, liquid-like phase that dissolves the salt precipitates produced in the upper (hot) reaction zone. This brine is removed continuously to prevent crystallization of salt on the reactor walls.

PFR — The PFR serves the same purpose as the CSTR, but is generally a very long, small-diameter tube. Rather than having different temperature zones in the PFR, solids management is controlled by fluid velocity. The linear velocity of the fluid always is kept above that which is required to suspend any resultant crystals in a slurry. In some schemes, mechanical action is used to enhance re-entrainment and to remove any sticky salt deposits that may have deposited on the surface. In a newer design, the reactor is fitted with small jets that transpire water through the reactor wall to create a boundary layer of relatively pure water to prevent attack from aggressive species and/or precipitation of sticky salts.

Leaving the reactor, the fluid phase products then are separated further from entrained solids, cooled down, and depressurized. Often heat recuperation or integration is used, where hot product effluent is cooled by incoming reactant streams to preheat the feed to reaction conditions. Such heat integration reduces the required heating value of the target waste fed to be self-sustaining. This autogenic condition corresponds to a state where the net heat of combustion per unit feed produces enough thermal energy to sustain the reaction without additional heating.

In certain applications, the process reactor is placed in a deep well with the reaction zone at the bottom of the well where supercritical pressures exist because of the hydraulic gradient. This concept has the advantage that the pumping power requirements are much less than for SCWO plants located on this surface.

Each portion of the flow sheet in Figure 1 is connected to one or more areas of research.

Feed Preparation and Pressurization — While the feed streams may seem inherently simple to handle, it is often necessary to estimate the fuel value of the target waste. Additionally, there is the strategy of pH control, which requires analysis of the feed for halogens, sulfur, and phosphorus; a corresponding amount of neutralizing agent may be added to the feed to promote effluent neutrality. There are also different methods of obtaining high concentrations of oxygen in the feed, using a pure oxygen feed or using hydrogen peroxide (H_2O_2), which catalytically decomposes to O_2 and water.[1]

Heat Exchangers — Heat exchangers are exposed to thermal and mechanical (pressure) load cycling, and are commonly the site of the most aggressive localized corrosion in the system. Current research aims at identifying thermodynamic (temperature [T], pressure [P], and composition [x_i]) boundaries for corrosion initiation in the preheater sections under acidic conditions.

Reactor — Upon entering the reactor, mixing of the feed streams takes place. As mixing time is an important parameter in determining reaction effectiveness, quantitative characterization of mixing rates have been conducted. In addition, reaction kinetics measurements also have been performed to determine overall "global" reaction rate expressions and to characterize reaction networks to illustrate how more rate-limiting or "refractory" compounds are produced as intermediates from the faster initial oxidation and/or hydrolysis of more labile compounds. Research to understand corrosion phenomena and thermodynamic factors promoting corrosion of the reactor wall and of heat-transfer surfaces also has been performed and will be discussed in a forthcoming paper.

Critical Engineering Issues Affecting Development

Key engineering issues affecting the commercial development of SCWO technology include salt and solids management, reaction rates, and materials performance.

Salt and Solids Management — Many of the feedstocks for SCWO produce insoluble salts. Corrosion and metals atoms in the feed stream also can produce insoluble oxides. While the oxides can be entrained by control of fluid velocity near process surfaces, the salts often are very sticky and tend to adhere to reactor walls and block the process streams.[2] Further, these entrained solids can cause erosion of process piping and valves.

Reaction Rates — Fluid density and solvent effects such as clustering can play a major role in reaction-determining reaction rates. Solution pH, a parameter often used in predicting and controlling corrosion, becomes difficult to measure or even define, as the ionic dissociation constant of water plunges near the critical point of water.[3] The water's dielectric constant, highly tunable across hydrothermal and supercritical conditions,[4] determines the ability of the medium to support polarized transition states, and therefore to support ionic reactions or reactions in which transition states have a large dipole moment.

Materials Performance — General corrosion or "wastage" occurs in the main reactor when aggressive feed stocks (containing S, P, and halogen [Cl, Br, F] atoms) are encountered. Corrosion-resistant alloys such as Inconel† 625 (UNS N06625)(2) and Hastelloy† C-276 (UNS N10276) have been observed dissolving at a rate of 740 mpy to 750 mpy (18.8 mm/y to 19.0 mm/y).[5] Worse, however, is the localized corrosion observed in the heat exchangers used for preheating and cooling of process streams. Localized attack, such as stress corrosion cracking (SCC) is difficult to detect because the amount of material lost is small. SCC is accelerated directionally as well as isolated to specific sites and quickly can cause through-wall failure.

Fundamental and Applied Research

SCWO technology provides an opportunity for significant process improvement utilizing insights obtained from fundamental and applied research. Reactor and process design technology of SCWO systems is hindered still by the sparsity of thermodynamic data for hydrothermal aqueous and supercritical solutions of salts and metal oxides and hydroxides.

A more fundamental understanding of the fluid mechanics and mass and heat transfer in such systems would aid in the development of mixing strategies, as well as the resolution of many key solids deposition and entrainment issues. Mixing effects can be critical for optimal reaction and residence

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(2) UNS numbers are listed in *Metals and Alloys in the Unified Numbering System*, published by the Society of Automotive Engineers (SAE) and cosponsored by ASTM.

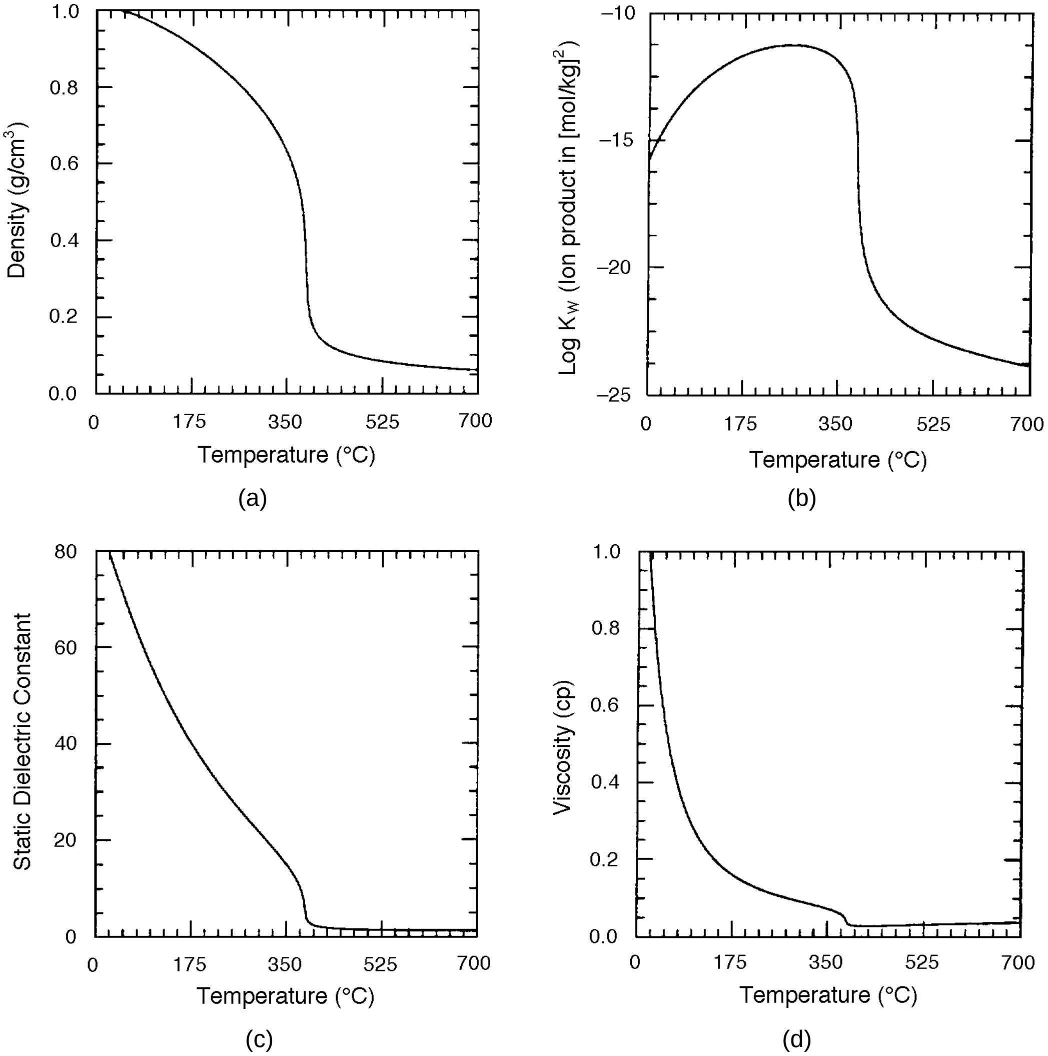

FIGURE 2. *Properties of pure water at 250 bar as a function of temperature.*

time-vessel reactors rely on convective transport to homogenize the reaction mixture, but residence times might be reduced if the manner in which the reactants are mixed as they enter the reaction vessel were optimized. A combined knowledge of heat transfer, convective, and forced flows, and salt solubility/deposition is required to prevent salt fouling of heat exchange surfaces.

Detailed molecular-level understanding of the reaction kinetics for the limiting reactions for a particular feedstock may lead to the development of reactors whose size and shape are optimized specifically for high conversion with proper solids handling appropriate to its task. Knowledge of the water chemistry produced by this feedstock and its products, in conjunction with an understanding of the thermodynamic stability limits of the reactor material (or its protective surface layer) will allow process designers to select materials based on cost, containment, and safety criteria for specific applications. Such kinetic and thermodynamic factors ultimately depend upon molecular-level interactions between the solvent and solute. Thus, improved understanding of these phenomena will augment the experimental criteria currently used to select equipment and set system design parameters.

ENGINEERING ISSUES AND TECHNICAL CHALLENGES

Water Chemistry

Behavior of K_w and D_s — Self-dissociation behavior and dielectric constant (D_s) drop off markedly in water at supercritical pressures as temperatures approach and exceed the critical point. As shown in Figure 2, at 250 bar, the dielectric constant of water drops from 80°C at 25°C to < 2 above 450°C. Also, at 250 bar, pK_w ranges from 14°C at 25°C to ≈ 22 at 450°C — an 8-order-of-magnitude change in the ion product $[H^+][OH^-]$ of water.

Aqueous Chemistry and Electrochemistry in SCW — Molecular simulations of solutions performed by Johnston and coworkers have investigated the pH and dissociation of boric acid (H_3BO_3) and sulfuric acid (H_2SO_4) at supercritical conditions.[6-7] This work has yet to be verified experimentally. Research continues for development of electrodes for electrochemical parameters in hydrothermal and supercritical water,[8-9] but the techniques have not been developed to a degree such that they are used widely. Work by Bard and coworkers have overcome numerous technical challenges (e.g., corrosion and electrode design) to explore some high-pressure electrochemistry of hydroquinone ($C_6H_4[OH]_2$) and iodide.[10] At temperatures up to 385°C, this work generated some measurements for diffusion coefficients in near- and supercritical water, as well as insight into the redox behavior of iodine and hydroquinone. From the magnitude of their diffusion coefficients, aqueous ions were found to exhibit normal Stokes-Einstein behavior.

Hydrogen Bonding — Another aspect of water that is markedly different at hydrothermal and supercritical conditions is hydrogen bonding.[11-24] Room temperature water has a radial distribution function (RDF) with many peaks (Figure 3), the structure of hydrothermal and supercritical water changes markedly with pressure and temperature.[25]

Solution Thermodynamics

Equations of State — Equations of state, which can predict the $PVTx_i$ behavior of SCW solutions, are needed to design and simulate process steps in SCWO. A volume-translated, hard-spheres, van der Waals equation of state was developed that accurately captures the density behavior of dense liquid and supercritical fluid phases.[26] Other, more complex equations of state are available, such as the one developed by Anderko and Pitzer for the NaCl-H_2O system.[27] These equations typically require fitting many adjustable parameters successfully has been used to represent a large amount of data. The SCWO community also has benefitted from the extensive work of geochemists, as much effort has gone into characterizing ionic solutions at hydrothermal conditions.[28-29]

Recent efforts have discovered a marked similarity between the Zeno line observed in high-density PVT data with predictions from equations of state and molecular dynamics simulations using an enhanced simple paint charge (SPC-E) water potential. The Zeno line is a locus of points in density-temperature space for which the compressibility factor (Z) of a fluid is again 1.0, similar to the ideal gas state, except the densities and temperatures are far from ideal gas conditions. Numerical simulations have been able to duplicate observed experimental Zeno behavior as closely as, or in some instances, more closely than other equations of state.

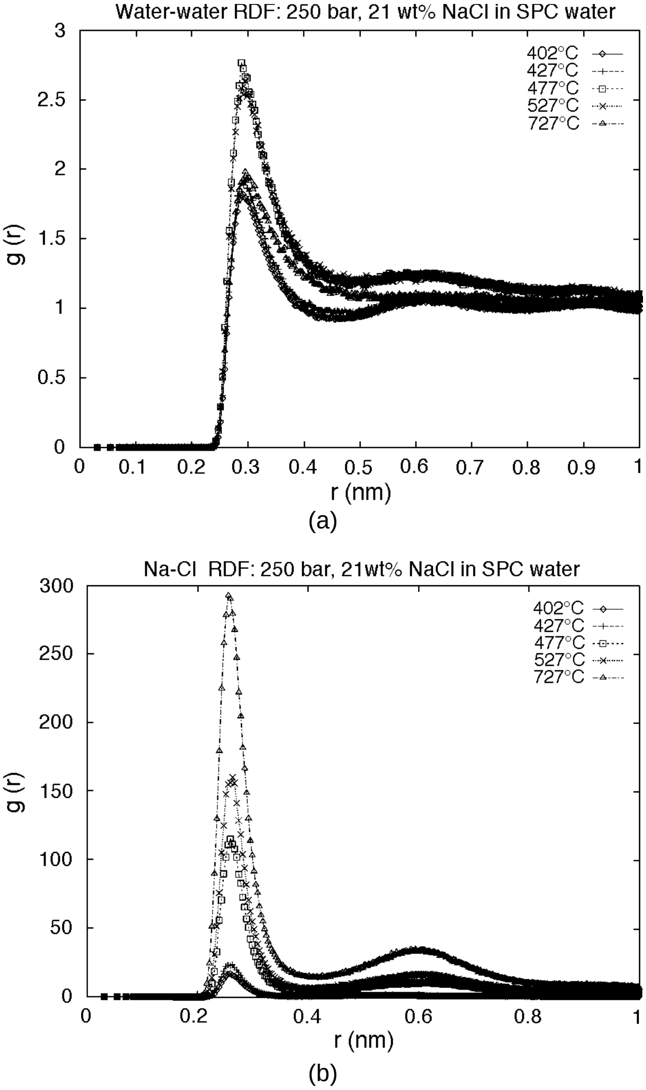

FIGURE 3. *(a) Water-water and (b) Na-Cl radial distribution functions, where g(r) is a function of separation distance, r, resulting from a molecular dynamics simulation of a 21 wt% NaCl-H_2O solution at 250 bar using the simple point charge (SPC) intermolecular potential model for pure water and a Huggins-Mayer plus coulombic and Lennard-Jones attraction potential for ion-ion interactions.*[25]

Molecular Simulations — The simulation of dense NaCl brine solutions at near and supercritical conditions using Monte Carlo and Molecular Dynamics has been an area of active research at MIT. Basically, the MIT research group is interested in exploring whether relatively simple intermolecular potential models for ion-ion and water-ion interactions can predict complex phase equilibria such as mixture critical points, phase transformations, and solid salt formation in supercritical water.[25] Figure 3(b) shows a typical RDF for Na-Cl over a range of conditions, where a strong tendency toward ion pair formation as temperature increases was seen.

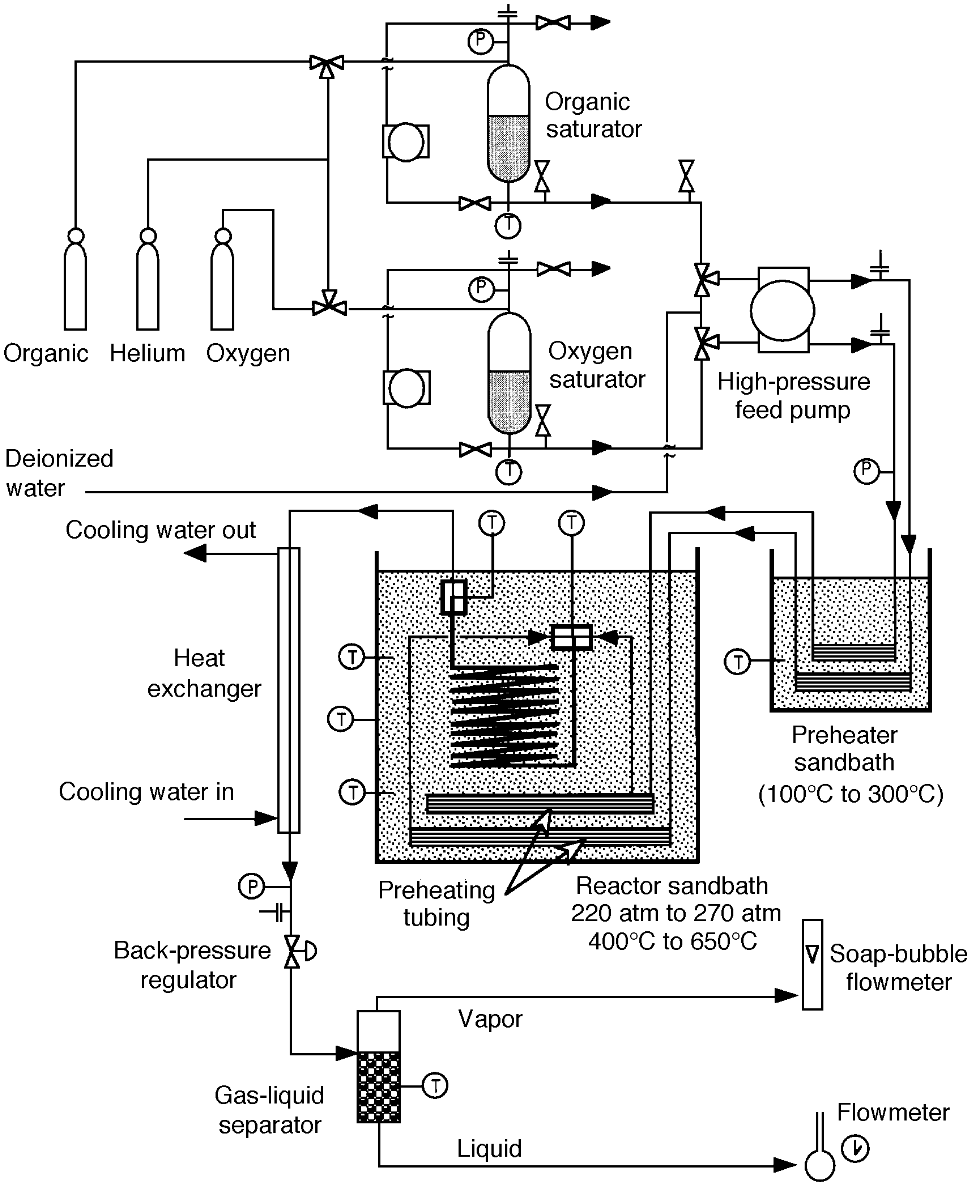

FIGURE 4. *Bench-scale apparatus for kinetic studies of hydrolysis and oxidation in a tubular PFR reactor system.*

Chemical Kinetics

Experimental Methods — Several groups performed kinetics experiments on model compounds in isothermal, isobaric plug-flow reactor (PFR).[30-39] The MIT group extensively used a PFR reactor system (Figure 4). Two feed streams (an aqueous oxygen stream and an aqueous model-compound-containing stream) flowed through separate preheaters into a mixing tee where the PFR began. The preheaters and tee were made of UNS N10276 and the PFR is made of UNS N06625. The preheaters and reactor (each coiled) were heated by immersion in a fluidized sand bath. After the reactor, flow proceeded to a shell-and-tube cool-down heat exchanger, then to a back-pressure regulator, and finally on to separators and analytical equipment.

Kinetics measurements using this apparatus were restricted to conditions in which the reactants were dilute enough that the reacting stream did not deviate measurably from isothermal conditions. Oxygen concentrations were limited by the amount of H_2O_2 added into the feed stream, as the H_2O_2 catalytically decomposes to O_2 and water, or in other configurations that use a O_2 saturator with concentrations set by the Henry's Law equilibrium of O_2 over water at room temperature.[35]

Experiments — Kinetic measurements were performed under conditions of controlled temperature, residence time, composition, pressure, and density (and, for catalytic effects, surface to volume ratio of reactor material UNS N06625) for various compounds, including C_6H_6, CH_3OH, phenol (PhOH), glucose ($C_6H_{12}O_6$), acetic acid (HOAc), ammonia (NH_3), carbon monoxide (CO), hydrogen (H_2), methyltertbutylether (MTBE), CH_2Cl, thiodiglycol ($[CH_2CH_2OH]_2S$).[34-39] Figure 5 illustrates the Arrhenuis behavior of first-order rate constants for several model compounds.

Elsewhere, numerous other oxidation kinetics studies have been performed, including studies of PhOH;[40] alkyl aromatics;[41] pulp and paper mill sludge;[42] methanol (MeOH), PhOH, methylethylketone (MEK), ethylene glycol (EG), acetic acid (HOAc), CH_2Cl_2 1,1,1-trichloroethane,[43] MeOH, ethanol (EtOH), and n-propanol; (n-PrOH)[44]; HOAc, NH_3,[45] TrimSol†;[46] 2,4-dichlorophenol;[47] p-nitroaniline;[48] isopropyl alcohol (i-PrOH);[49] CH_4 to MeOH;[50] methylphosphonofluoridic acid 1-methyl-ethyl ester (GB), methylphosphonothioic acid S-[2-[bis(1-methylethyl) amino] ethyl] O-ethyl ester (VX), mustard ($[ClCH_2CH_2]_2S$);[51] and hydroquinone (1,4-benzenediol).[52]

While many of the initial kinetics investigations were studies of global destruction rates of target waste mixtures (such as sludges, solid rocket propellants, and chemical weapons agents), later studies tended to focus mostly on single-model compounds under very narrowly controlled reaction conditions. The model compounds chosen were those which were more refractory, and thus rate-limiting in the overall oxidation process, and included C_6H_6, HOAc, formaldehyde (HCHO), CH_4, and NH_3, and their related products, H_2, and CO. Specific attention is given to the extent of catalytic effect exerted by the reactor walls (often UNS N06625 or UNS N10276), the determination of global rate laws, and chemical pathways for hydrolysis and oxidation.

Kinetics Modeling — Oxidation reactions at high temperatures often are modeled using traditional combustion-free radical reaction networks. This approach has been adapted to model oxidation at the high densities in SCWO systems. In particular, reactions between water and related free radicals are now very significant, as water is the primary third-body collider. Also, radical quenching can be important. A key issue in free-radical modeling involves determining the important reactions and species in networks that potentially can have hundreds of reactions. In addition, developing a quantitative appreciation for the effects of uncertainties in specified elementary reaction rate constants and thermochemistry on global oxidation rates is crucial.

Often at SCW conditions, the data needed to support free-radical modeling are incomplete, making quantitative predictions untractable. Nonetheless, fundamental knowledge of the reaction system can be of great value in providing estimates. An alternative approach is to consider lumped macroscopic reaction steps. A case in point is the S_N2 hydrolysis reaction of CH_2Cl_2 with water, where the only previous experimental data was limited to conditions at 80°C to 150°C in liquid water.[53] When these data were extrapolated to supercritical conditions, there was a wide disparity with new experimental data. This disagreement between extrapolated and measured reaction rates is the direct result of a change in the medium properties and can be quantitatively described with a theory developed by Kirkwood.[54]

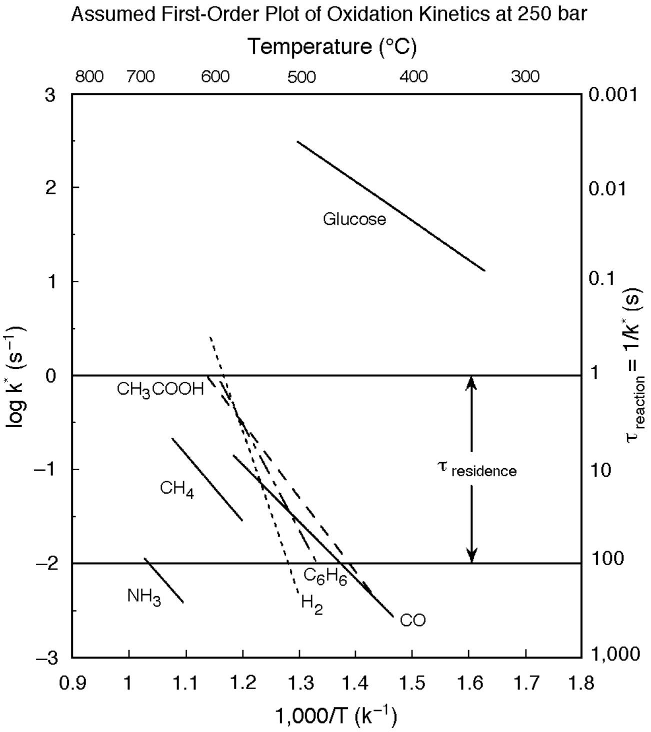

FIGURE 5. *Arrhenius behavior of first-order oxidation rate constants for several model compounds in supercritical water. An assumed first-order constant (k*) is calculated from experimental conversion data at a specified temperature and residence time ($\tau_{residence}$) at a pressure of 246 bar. The characteristic reaction time ($\tau_{reaction}$) is defined 1/k*.*

Effects of Medium — Hydrolysis and oxidation reactions are sensitive to the density of their molecular environment. Effectiveness of intermolecular interactions between the solvent and reactants influences the rates of hydrolysis and oxidation reactions. To resolve the aforementioned disparities between measured CH_2Cl_2 hydrolysis rates and extrapolations from published data, the effect of changes in solvent properties was investigated. Theory developed by Kirkwood relates the Gibbs free energy of activation (used in conventional transition state theory) to the radii and dipole moments of the transition state complex, reactants, and products, and to the solvent's dielectric constant.[54] Estimates for the transition state dipole moment and radius then were derived by computing the transition state charge density distribution using ab-initio methods.[55] By compensating for the effect of the medium on the free energy

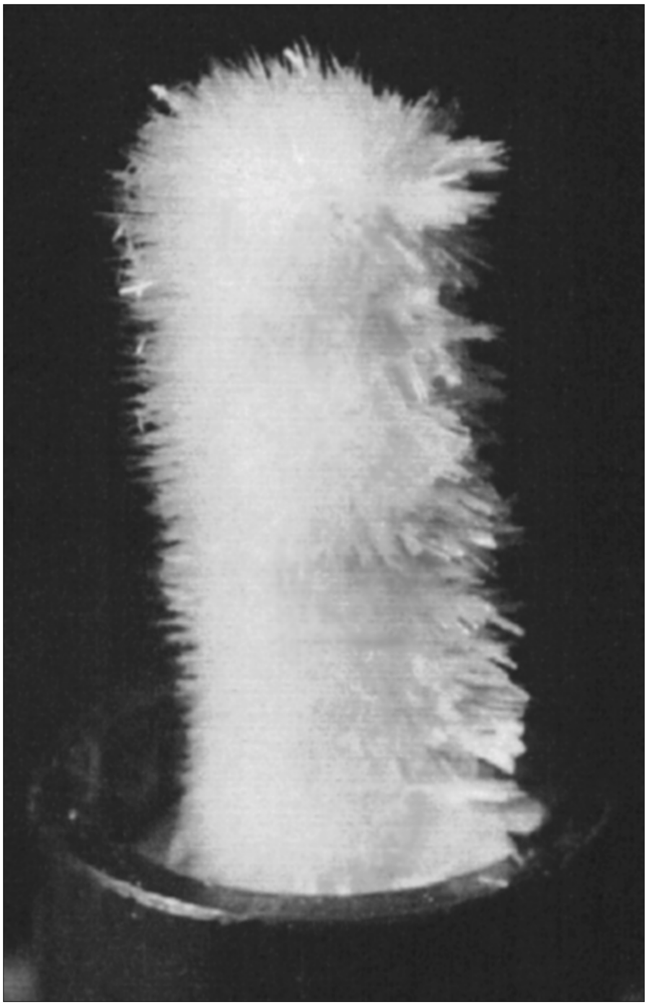

FIGURE 6. *Potassium sulfate (K_2SO_4) salt deposits formed at supercritical conditions (T > 374°C, P = 250 bar) in laminar flow from a 4 wt% K_2SO_4 solution.*

of the reaction transition state, the disparity between measured and predicted hydrolysis rates based on extrapolating low-temperature rate data was resolved.

A more rigorous study by Arias, Marrone, and Reagan is underway that places the electron density distribution of the transition state (from the previous ab-initio study) into a molecular dynamics simulation using SPC water molecules. Here, the average inhomogeneous dielectric structure of the fluid could be approximated rather than assuming a constant dielectric environment for the medium. Another similar study was pursued by Pomelli and Tomasi focusing on methyl chloride (CH_3Cl), but using quantum mechanical methods more extensively.[56]

Another consideration is the role of the reactor materials themselves on reactions, which might catalyze or poison the reactions. Investigations by Webley, et al., compared results from UNS N06625 PFR and packed-bed reactors to show that ammonia oxidation is sensitive to the extra surface area in the packed bed, while CH_3OH and CH_4 oxidation rates were independent of surface area effects over this range.[34-35,57] Holgate, using the same apparatus, later showed that CO and H_2 oxidation is slowed by the extra surface area, probably through termination of free-radical species.[37,39]

Macrotransport Rates

Salt Deposition — Metal oxides and salts are two main categories of insoluble inorganic compounds, which are produced during SCWO. The metal oxides come from the feed stream, which may contain metals, or from the reactor wall, where corrosion has taken place and the oxide has become detached. These solid metal oxides are generally brittle and relatively inert chemically and easily are entrained in the process stream (particularly in PFR-type systems). The salts, in contrast, can be very sticky, and under prevailing supercritical process conditions, are relatively insoluble.[2] These sticky salts can hinder heat transfer, harbor corrosive agents, and tend to aggregate and obstruct flow.

A collaboration between MIT and the National Institute for Standards and Technology (NIST) focused on describing the deposition of salt in supercritical water under simulated SCWO process conditions.[58] Experiments at NIST examined the behavior of an immersed, heated cylinder exposed to a constant flow of salt-containing supercritical water to study salt deposition on a surface (Figure 6). Here, deposition kinetics and morphology were related to diffusion and convective transport phenomena.

Diffusion and Mixing — In a separate study, the use of nuclear magnetic resonance (NMR) imaging to quantitatively capture molecular and bulk fluid motion in supercritical water is being explored. This method has the advantage that it is completely non-intrusive. Using a gradient field, pulsed NMR approach, an electromagnetic signature is assigned to the water molecules in arbitrarily thin cross sections of a control volume at an initial time. These signatures are tracked as time evolves to measure the rate of displacement to determine molecular diffusivities or to determine fluid velocities in a two-dimensional (2-D) cross section.

Materials Performance

Key Issues — In general, materials of construction for SCWO systems must be able to withstand high temperatures, high pressures, and corrosive process streams. Heat-transfer media additionally must be able to withstand the thermal stresses induced by large temperature changes. Proper selection of materials, from performance-oriented and economical points of view, requires an understanding of the rates and mechanisms of corrosion and erosion, and how adaptations in the process conditions may be able to sustain materials performance at acceptable levels.

General Corrosion/Wastage — In the presence of more "aggressive" feedstocks (i.e., compounds containing halogens, sulfur, and/or phosphorus), significant general corrosion can take place.[59] During corrosion tests at MODAR[†] (now General Atomics) using a halogenated mixed solvent, TrimSol[†], as the feedstock, Mitton, et al., exposed coupons of various alloys to the environment for 66.2 h, and found high general corrosion rates (e.g., 2,000 mpy [50.8 mm/y]) for type 316L (UNS S31603), 740 mpy to 750 mpy (18.8 mm/y to 19.0 mm/y) for UNS N06625 and UNS N10276). Metallurgical and electrochemical analysis of these coupons was presented in another paper.[60] Ceramics are not immune to attack either. Research of Boukis, et al., investigates corrosion of zirconia ceramics in the presence of mineral acids[61] and le Clerq[62] describes attack of supercritical seawater on an alumina-lined reactor.

With sufficient thermodynamic data, corrosion engineering in SCWO systems may be simplified by the generation of Pourbaix diagrams. To produce Pourbaix diagrams of SCWO systems, thermodynamic data must be extended into higher temperature and pressure regimes. Huang, et al., derived methods for such extensions, and identified the requirement for heat capacity data (for entropy contribution) and enthalpy data (explicitly or using heat capacity, thermal expansivity and isothermal compressibility) to obtain the free-energy change of reaction at hydrothermal temperatures and pressures.[63] Kriksunov and MacDonald combined this approach with the Helgeson-Kirkham-Flowers (HKF) equation of state (EOS)[27-29] to more accurately determine the Pourbaix diagram for metals in SCW.[64]

Localized Corrosion — Generally, it has been noted that the worst corrosion in SCWO systems occurs in the heat exchangers, where the fluid is hot but subcritical and can sustain ionic reactions.[59,65-66] In the heat exchangers, the dominant mode of corrosion observed is localized, usually as SCC. Mitton, et al., examined multiple through-wall preheater failures generated during the MIT group's CH_2Cl_2 experiments.[67] As these failures occurred in acidified streams, pH and water chemistry control was recommended.[67] Localized corrosion is difficult to detect and quantify, as only a very small amount of material actually is removed before the process piping is compromised, but because of locally accelerated rates, failure can occur very rapidly.

Erosion — Entrained solids (oxides, salts) can erode process piping, particularly at bends, valves, and other discontinuities. These effects are exacerbated when the materials of construction obtain their corrosion resistance by maintaining a passive layer, as this will be the first component to erode continually, providing a fresh, bare metal surface for oxidation.

RESEARCH NEEDS

Density Effects on Reaction Rates/Mechanisms

Density of the medium may have a strong effect on chemical reaction rates, not only by concentration of specific reactants in the system, but also through changes in dielectric constant and therefore the ability of the medium to sustain dipoles and/or ionic charge separations. Another density effect is that of the water medium as a "third body" for reactions, which, in conjunction with molecular cage effects, would promote deactivation of active species. Also, under SCWO conditions, water itself is a reactant, and as such can contribute significantly to the free-radical pool and will promote reactions that require water or consume water reaction by-products.

Electrochemical Data for Hydrothermal Salt Solutions (P > 25 MPa and T > 300°C)

The majority of the corrosion data for high-pressure steam systems lie < 300°C. By obtaining and using data and/or equations of state for conditions > 300°C, Pourbaix diagrams relevant to SCWO systems can be generated, which vastly would expedite the selection of proper combinations of materials and water chemistries for best materials performance. Work by MacDonald, et al.,[64,68-69] uses the data of Helgeson, et al.,[28-29] (Tanger paper is a revision of the HKF EOS), from the HKF equation of state for hydrothermal systems, to predict the Pourbaix diagram for iron > 300°C, without requiring approximations such as the Criss-Cobble entropy correspondence principle.[70]

To this end, there is a need for widely available pH and reference electrode technology,[8,10,71-73] which repeatedly can withstand SCW operational conditions. Once more widely available, electrochemical impedance spectroscopy and other modern tools of electrochemistry can be used to map out the stabilities of various materials under a wide range of operating conditions and chemistries.

Pourbaix Diagrams for Alloys

The majority of Pourbaix diagrams available are for single-element systems. As a first approximation, a pseudo-pure component approach can be applied to multicomponent alloys, but the properties of atoms in alloys are most often different from pure component behavior. However, as yet, there is no general work for Pourbaix diagrams that include non-ideal effects of alloying, such as incorporating models for activity coefficients of the alloyed elements explicitly.

Molecular Modeling of Solvation, Corrosion Initiation, Metal-Ion Interactions

Numerous molecular dynamics simulations have explored the fundamentals of ion solvation[11,14,25,74-76] and hydrogen bonding[16,20-21,23,25] in supercritical water, and, in many cases, have been able to provide semi-quantitative information regarding solvation structure, including solvation and clustering in sub- and supercritical water (Figure 3[b]).

But molecular modeling can be extended, for instance, to examine transition states for reactions other than CH_2Cl_2 hydrolysis in various solvent environments for detailed reaction modeling. A fuller understanding of solvation and solvent cage effects can be used in modeling the effectiveness of collisions between reacting species. Further, models that take into account interactions between the aqueous ions and the metal reactor walls, for purposes of catalysis or corrosion modeling, are needed.

In-Situ Process Diagnostics

Spectroscopy — Spectroscopy can be used to measure directly concentrations of reactants and sizes and populations of particulate matter, as well as to characterize solvation dynamics, clustering, and or structural changes induced by reactant-solvent interactions. Steeper and Rice used Raman spectroscopy to measure concentrations of CH_4, O_2, N_2, CO, and CO_2 in situ during SCWO of CH_4.[77] Johnston and coworkers have used absorption spectra to probe pH in water at conditions of ≈ 350°C and 240 bar, using indicators such as 2-naphthol.[6] A broader extension of spectroscopic methods would benefit industrial applications by providing detailed data regarding the progress of the reaction, perhaps changes in water chemistry relevant to corrosion control. Another relevant application is determination of particle size distributions using dynamic light-scattering techniques. Such methods can be used to characterize nucleation and growth kinetics of the insoluble species.

Electrochemical Noise Analysis — Electrochemical noise analysis is being investigated as a means to detect corrosion in situ.[71,78] Such analysis would provide a valuable tool from a safety and operational standpoint, as engineers could monitor systems continuously to assess corrosion effects.

Other descriptions of research needs can be found in the literature.[36,65]

CONCLUSIONS

❖ In this review, the vital importance of connecting process engineering science to molecular-level effects to improve the performance of SCWO as a practical waste treatment and remediation technique was explored.

❖ Although the basic science elements of chemical reactions and phase transformations in supercritical water are of general interest by themselves, the application of fundamental knowledge obtained from well-defined experiments and macrotransport and molecular modeling has had a direct impact on process selection and performance enhancement.

❖ The range of future opportunities for research in this area is vast — from hydrothermal solution thermodynamics and kinetics to molecular modeling of metal-ion and water-ion interactions.

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