

REVIEW OF MATERIALS ISSUES IN SUPERCRITICAL WATER OXIDATION SYSTEMS AND THE NEED FOR CORROSION CONTROL

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ABSTRACT

As the World's population continues to grow, technology must be developed to treat wastes of all kinds, and at the same time the energy demand of this increasing population must be met. In both cases waste treatment and energy conversion must be performed with increasing attention to air and water quality on the Earth. Supercritical water (SCW) systems have the potential to address these problems in an environmentally sound way.

Supercritical water oxidation (SCWO) is a promising technology for destroying highly toxic organic compounds present in aqueous waste streams. Capitalizing on the properties of water in the supercritical regime (above 647 K and 22.1 MPa for pure water), spontaneous and rapid oxidation of hydrocarbons is obtained with a very high efficiency, forming water, carbon dioxide, and—depending on the species of heteroatom present in the organic waste—one or more acids. The extreme operating conditions (i.e., the presence of acids under highly oxidizing conditions in SCWO feeds, high temperatures and high pressures), however, require identification and/or development of constructional materials that are capable of withstanding such an environment.

This presentation reviews the advantages of the SCWO technology as well as some major concerns related to the selection of constructional materials and to the control of corrosion in this environment. The degradation characteristics of several candidate constructional materials, including iron-, nickel- and titanium-base alloys, ceramics and noble metals are described. In addition, a number of potential methodologies for reducing corrosion damage in SCWO systems are discussed.

1. BACKGROUND

There is a need to destroy both military and civilian hazardous waste. The Chemical Weapons Convention (CWC), for example, which was signed by 130 countries in January 1993, seeks to eliminate chemical weapons and their production early in the new millennium. Public concern over traditional waste handling methodologies such as landfill or incineration has led to special efforts in identifying environment-friendly, safe, efficient and economic alternative technologies. One very effective process for the destruction of such waste is SCWO, which capitalizes on the properties of water above its critical point.

From performance point of view, constructional materials for SCWO systems must be able to withstand high temperatures, high pressures, and corrosive process streams. Heat-transfer media must also be

able to withstand the thermal stresses induced by large temperature changes. Entrained solids such as oxides and salts might erode the piping and valves. Moreover, the salts are often very sticky and tend to adhere to reactor walls and block the process.^{1,2} Nevertheless, corrosion of the constructional materials is probably the main limiting factor in the commercialization of the SCWO technology. General corrosion, or wastage, occurs in the main reactor when aggressive feed stocks (containing sulfur, phosphorus and/or halogen atoms) are encountered. Otherwise corrosion-resistant alloys such as Inconel 625 and Hastelloy C-276 have been observed dissolving at a rate of 740 to 750 mpy (18.8 to 19.0 mm/y). 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, and might quickly cause through-wall failure.¹

In addition to destruction of hazardous waste, interest in supercritical (SC) light water as the coolant in a direct-cycle nuclear reactor has recently emerged. SCW offers potential for considerable plant simplification and consequent capital, operation and maintenance cost reduction compared with current light water reactor (LWR) designs. Also, given the thermodynamic conditions of the coolant at the core outlet (i.e., temperature and pressure beyond the water critical point), very high thermal efficiencies of the power conversion cycle are possible (up to 46%). Because no change of phase occurs in the core, the need for steam separators and dryers as well as for BWR-type recirculation pumps is eliminated, which, for a given reactor power, results in a substantially shorter reactor vessel than the current BWRs.³⁻⁵ This application of SCW also requires selection of constructional materials that will be able to perform well under an extreme environment. The rest of this paper, however, will focus on the properties of SCW and the corrosion issues encountered in SCWO systems.

2. THE PROPERTIES OF WATER IN THE SUPERCRITICAL REGIME

The properties of pure water change dramatically as its critical point (647K, 22.1 MPa) is approached. At the critical pressure, there is no constant-temperature vaporization process. The critical point implies that the saturated liquid and saturated vapor states are identical (i.e., at pressures above the critical pressure we never have a liquid and vapor phase of a pure substance existing in equilibrium). Under SC conditions, the density of water is approximately 100 kg m⁻³, between that of liquid (1000 kg m⁻³) and low-pressure vapor (<1 kg m⁻³) water. Near the critical point, these drastic changes in the density of water correlate directly with drastic changes in its solvation properties. Water's ability to shield charge diminishes as its dielectric constant decreases from 80 at ambient conditions to ~2 at 25 MPa and 673K. At the same time, the ionic dissociation constant decreases from 10⁻¹⁴ at room temperature to 10⁻²³ at SC conditions. Consequently, low-density SCW acts as a non-polar dense gas with solvation properties

approaching those of a low-polarity organic. Hence, SCW exhibits high solubilities for non-polar organic compounds and non-condensable gases. For example, benzene (C₆H₆) is completely miscible in water above 573 K and 25 MPa over all concentrations.^{6,7} Gases such as oxygen (O₂),⁸ nitrogen (N₂),⁹ carbon dioxide (CO₂)¹⁰ and methane (CH₄)¹¹ are also completely miscible in SCW. Conversely, the solubility of inorganic salts is very low in SCW. For example, the solubility of NaCl in water at 25 MPa drops from about 37 wt% at 298K to only 120 ppm at 823K. Figure 1 is a schematic representation of the change in the solubility of organic and inorganic materials as well as the fluid density in the vicinity of the critical point.¹²

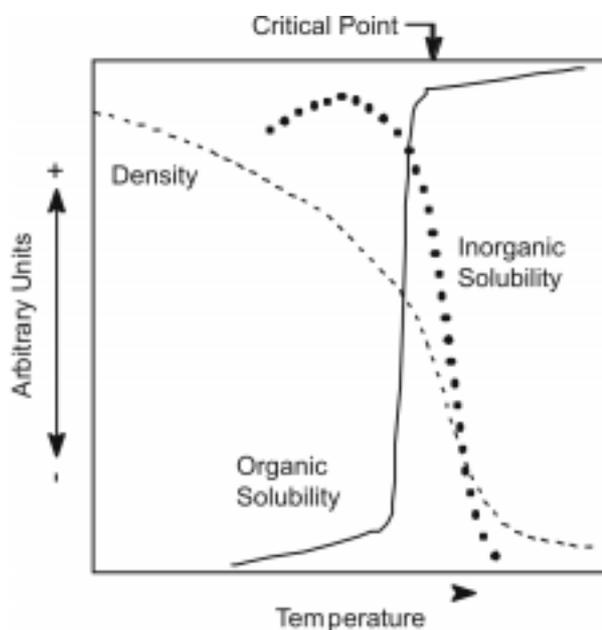


Fig. 1 : A schematic representation of the change in the solubility of organic and inorganic materials as well as the fluid density in the vicinity of the critical point.¹²

3. SUPERCRITICAL WATER OXIDATION (SCWO)

Over the last twenty years, SCW has found numerous applications as an aqueous medium for different processes, including chemical reactions, extractions, ceramic processing, analytical applications, biomass conversion, and the destruction of hazardous organic wastes. The chemical process that brings about the destruction of the organic waste is governed by an oxidation reaction, thus this process is known as

SCWO. SCWO systems provide high destruction efficiencies for organics within short residence times. Typical destruction and removal efficiencies (DRE) can exceed 99.999% for normal operating conditions of 25 MPa, 873 K, and residence times of 60 s or less. These efficiency levels meet the requirements of the Environmental Protection Agency (EPA) and the Department of Defense (DOD). The SCWO process is an entirely self-contained closed-cycle operation, precluding any exposure of hazardous materials to the surroundings and allowing for the capture and storage of reaction products for analysis and further treatment.

The SCWO process can be effectively used to treat organics present in dilute aqueous waste streams, the disposal of which is of great interest to the U.S. government. The destruction of EPA's regulated wastes, Department of Energy (DOE's) and DOD's stockpiled wastes are all promising applications for SCWO. Specific applications sited for the SCWO process in the U.S. are the destruction of solid rocket propellants, explosives, organics present in low-level liquid radioactive wastes, and chemical warfare agents.¹³ NASA has also investigated SCWO for use in remediation of biomass and human metabolic waste for long-term space flight.¹⁴ Germany and Japan have targeted various industrial aqueous toxic wastes for destruction by SCWO.^{15,16}

The process steps and possible setups for SCWO have been described by Cline comprehensively.¹⁷ Typically, a SCWO process begins with two or three aqueous feed streams—an oxidizer stream, an organic waste stream, and possibly an auxiliary fuel stream. The SCWO feeds are initially pressurized from ambient conditions to the operating pressure of the reactor and then pumped through a heat exchanger, where they are preheated to the desired SC temperature. Depending on the specific design of the system, these feed streams may be brought up to pressure and preheated before or after mixing. In either case, the combined reactant streams enter the main reactor in the SC state. The reactor may be either a vessel reactor or continuously fed stirred-tank reactor (CSTR), or a tubular plug-flow reactor (PFR). The vessel and continuous stirred-tank reactors are vertically oriented and employ two major temperature zones, which are designed to facilitate solids handling and mitigate corrosion. The top temperature zone is

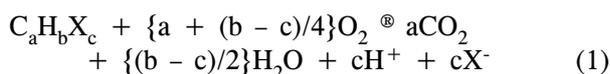
the hot reaction zone. This high temperature zone, which operates entirely under SC conditions during SCWO processing, is maintained at a nominally constant pressure, with temperatures ranging from 673 to 923K. Most of the oxidation of the organic waste takes place in the top temperature zone, producing mainly CO₂, H₂O, and— depending on control of pH in the feed stream—acids and inorganic salts. The lower temperature zone is maintained within a lower subcritical temperature range and a correspondingly higher fluid density. Vertical separation between the top temperature zone and the lower cooler zone are a result of buoyancy forces, which arise from a difference in fluid density between the top high temperature zone and the lower cooler zone. Mixing within the reactor is facilitated by buoyancy forces arising from large differences in the local fluid density within the top temperature zone. Low-density fluid phase products are carried upwards through an exhaust port. At higher feed stream pH values, the SCWO of organic compounds will produce inorganic salts. In the hot reaction zone these salts will precipitate out of the SC phase and settle into the lower, cooler zone, where the subcritical fluid redissolves the salt into dense liquid phase brine. The brine phase is continuously removed to prevent crystallization of salt on the reactor walls. Leaving the reactor, the SC fluid effluent is screened for solids, cooled in a heat exchanger and depressurized. The cool-down heat exchanger recovers heat from the effluent, which can be used to preheat the feed, or potentially – to produce steam for electric power generation.¹⁸ The spontaneous SCWO of the organic waste in the reactor can potentially produce heat in excess of that required to preheat the feed. Therefore, influent reactant streams may be used to cool the hot product effluent streams through the use of one heat exchanger that integrates the steps of influent preheating and effluent cool-down. This process produces sufficient thermal energy in the influent to sustain the SCWO reaction without the need for preheating by an external source. Thus, the SCWO process is capable of operating under self-sustaining conditions.¹⁹

SCWO is one potentially promising technology applicable to many organic wastes and has been shown to be well suited for handling dilute wastes in the range 1-20%, which are not suitable for disposal by

either incineration or landfill. High destruction efficiencies are possible for temperatures above approximately 823K, even for short reactor residence times. An additional benefit is that, as a result of the relatively low operating temperature, NO_x and SO₂ compounds are not produced. The latter may be particularly important during the destruction of explosives, which produce nitrogen oxides during incineration.^{20,21}

4. CORROSION - A MAJOR OBSTACLE TO IMPLEMENTATION OF SCWO TECHNOLOGY

The major disadvantages of the SCWO technology revolve around the high pressures and temperatures in operation, potential inorganic solids handling problems, and for most waste streams - corrosion of the system's constructional materials. Corrosion represents the greatest obstacle to successful implementation of SCWO. Chemically aggressive environments arise primarily as a result of the formation of acids under highly oxidizing conditions during the oxidation of hydrocarbons. Moreover, the SCWO reactor utilizes a high partial pressure of oxygen in order to achieve rapid oxidation of the organic waste, giving rise to conditions that are highly oxidizing. Kriksunov and Macdonald have suggested a typical reaction scheme for the oxidation of an organic compound in the SCWO process:²²



In this reaction, C_aH_bX_c represents a simple hydrocarbon and X represents the heteroatom, which may be a halogen atom such as fluorine (F) or chlorine (Cl). When the hydrocarbon oxidation reaction takes place, the halogen (X) converts to halide (X⁻), which can persist as an acid in the fluid phase. Thus, from a corrosion standpoint, the SCWO reaction results in the formation of innocuous byproducts (CO₂ and H₂O), as well as potentially aggressive species (H⁺ and X⁻) which represent the dissociated generic acid (HX) in solution. Non-halogen heteroatoms, including sulfur and phosphorous, can also be present in the organic waste compound. Thus, the anion X⁻ may also represent sulfate (SO₄²⁻) or phosphate (PO₄³⁻) ions in actual SCWO applications.

By all standards, the SCWO process environment is the most aggressive yet encountered from a materials degradation standpoint. This is due to the formation of acids under highly oxidizing conditions in hydrothermal aqueous environments. Corrosion control cannot be effectively achieved under such conditions through design and/or materials selection alone. Figure 2 shows the phase stability diagram for iron in water at 673K and 50 MPa.²³ The two shaded regions indicate the regions in potential-pH space where SC thermal power plants and SCWO systems operate under the SC conditions given above. It is evident that SCWO systems are exposed to much severe conditions of corrosion, as reflected by the lower pH values and the higher oxidizing potentials. It should be noted that the development of techniques for measuring pH, oxygen content, hydrogen content,

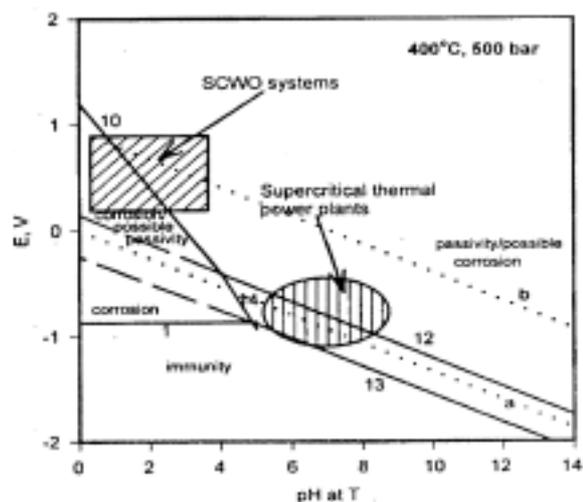


Fig. 2 : Phase stability diagram for iron in water at 673K and 50 MPa.²³ The two shaded regions indicate the regions in potential-pH space where SC thermal power plants and SCWO systems operate.

and redox potentials in SC aqueous environments is highly challenging. The development of methodologies for on-line monitoring of the chemical and electrochemical conditions in SCWO process environments is important for effective corrosion control based on thermodynamic considerations. Macdonald and Kriksunov applied measurement techniques to high subcritical and SC aqueous solutions at temperatures as high as 803K.^{23,24} The standardization of pH and the development of a viable pH scale in SCW were addressed as a means of providing a reliable and accurate assessment of pH conditions in the SC regime. It is evident, however,

that most studies to date have focused on the subcritical regime. Such studies are still valuable as the most severe corrosion attack has often been observed in SCWO heat exchanger tubing where temperatures are high, but subcritical. This could be related to a competition between two factors: the Arrhenius behavior of corrosion reactions rates, and the reduced concentrations of the aggressive species H^+ and O_2 with increasing temperatures as a result of decreasing water density and acid dissociation.

5. THE STUDY OF CORROSION UNDER SCWO ENVIRONMENTS

A number of different experimental setups have been employed specifically for studying the corrosion performance of candidate SCWO constructional materials. Figure 3 presents a schematic representation of the current SCW facilities in the Uhlig Corrosion Laboratory at MIT. The exposure facility incorporates a relatively large autoclave (Fig. 4) with an internal

volume of approximately 0.86 l. It is large enough to expose a rack of samples (weight loss, welded, U-bend) for extended times. The high-pressure liquid chromatograph (HPLC) pump is capable of a maximum flow rate of 0.1 l per minute. The preheater water and corrosive (generally HCl) are typically maintained separately until after the DI water feed is heated to SC. The reason for this is that we have observed a correlation between temperature, corrosion rate and corrosion mode, with the worst corrosion associated with a high subcritical temperature. For safety, both exposure and instrumented tube facilities are in individual lexan enclosures, and control (LabVIEW) is from outside a restricted area. All lines have rupture disks as well as pressure and temperature controllers, and the computer will compensate in the event of a pressure or temperature extreme. Compensation involves turning off the heater or the pump, or in a very extreme situation – the system will be entirely shut down. Subsequent to an exposure test, samples are

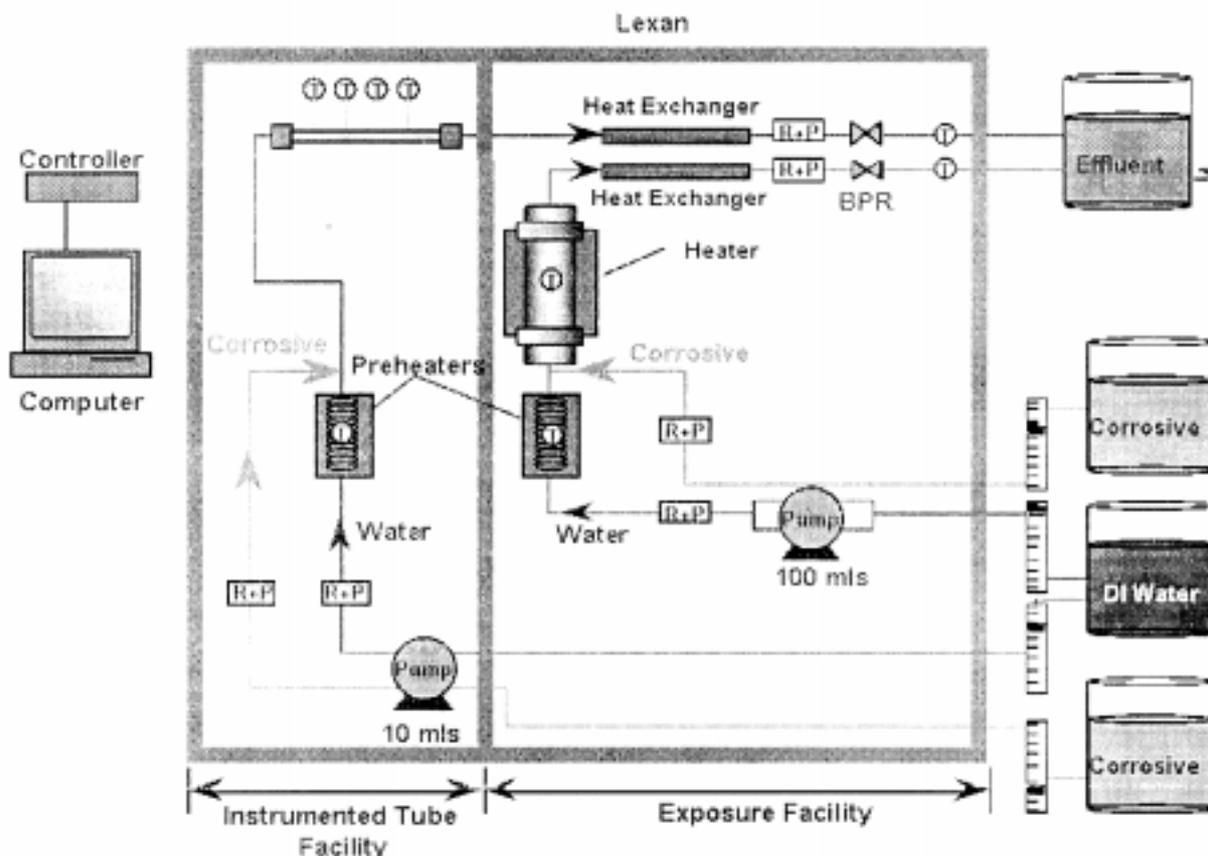


Fig. 3 : Schematic of the MIT supercritical water loop.

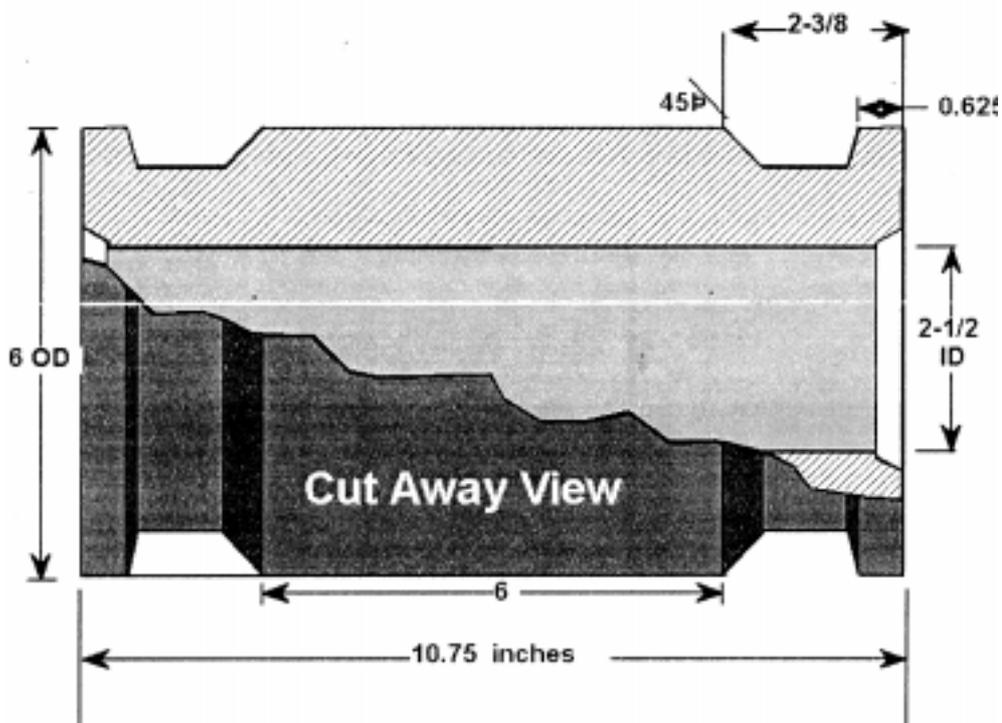


Fig. 4 : Schematic of the MIT autoclave.

examined metallographically and analytically to assess the corrosion rate and mode. While only one temperature and feed condition may be tested during each individual exposure, multiple materials can be evaluated.

As mentioned above, previous research at MIT has indicated a correlation between temperature and degradation for SCW systems. Therefore, it is considered important that potential materials be assessed in the most aggressive temperature range. In order to define this temperature range, initial testing can be accomplished with an instrumented autoclave design (Figs. 3 and 5), which has successfully been employed in the Uhlig Corrosion Laboratory. This design permits simultaneous exposure of a single material (a tube or a wire) to multiple temperatures. The feed is heated to the temperature of interest by pumping it through a preheater located just prior to the autoclave. Thermocouples are spaced equidistantly, and the temperature decreases along the length of the autoclave, with the highest temperature at the inlet. The output from each thermocouple is monitored and recorded throughout the test; thus, the corrosion mode and extent can ultimately be correlated to temperature. The fluid flows out of the top of the

autoclave and is directed through a cool-down heat exchanger before passing through the back-pressure regulator (BPR) and into a collection carboy.

6. CORROSION OF VARIOUS CONSTRUCTIONAL MATERIALS IN SCWO ENVIRONMENTS

6.1 Iron-Base Alloys

In general, except for innocuous feed streams, alloys such as 316L stainless steel are unlikely to be employed during fabrication of a SCWO waste treatment unit. Such alloys have generally been included in a test matrix as a baseline material. When exposed to DI water within the temperature range 573-773K, 316L may reveal excellent general corrosion and overall performance. Alternatively, localized effects such as pitting, intergranular corrosion (573K) or crevice corrosion (773K) might be seen. Within a restricted pH range (~2-11) and for an influent with minimal Cl content, 316L may exhibit reasonable performance and a uniform corrosion rate as low as 0.035 mmpy; however, even for a restricted Cl feed, SCC might be observed at

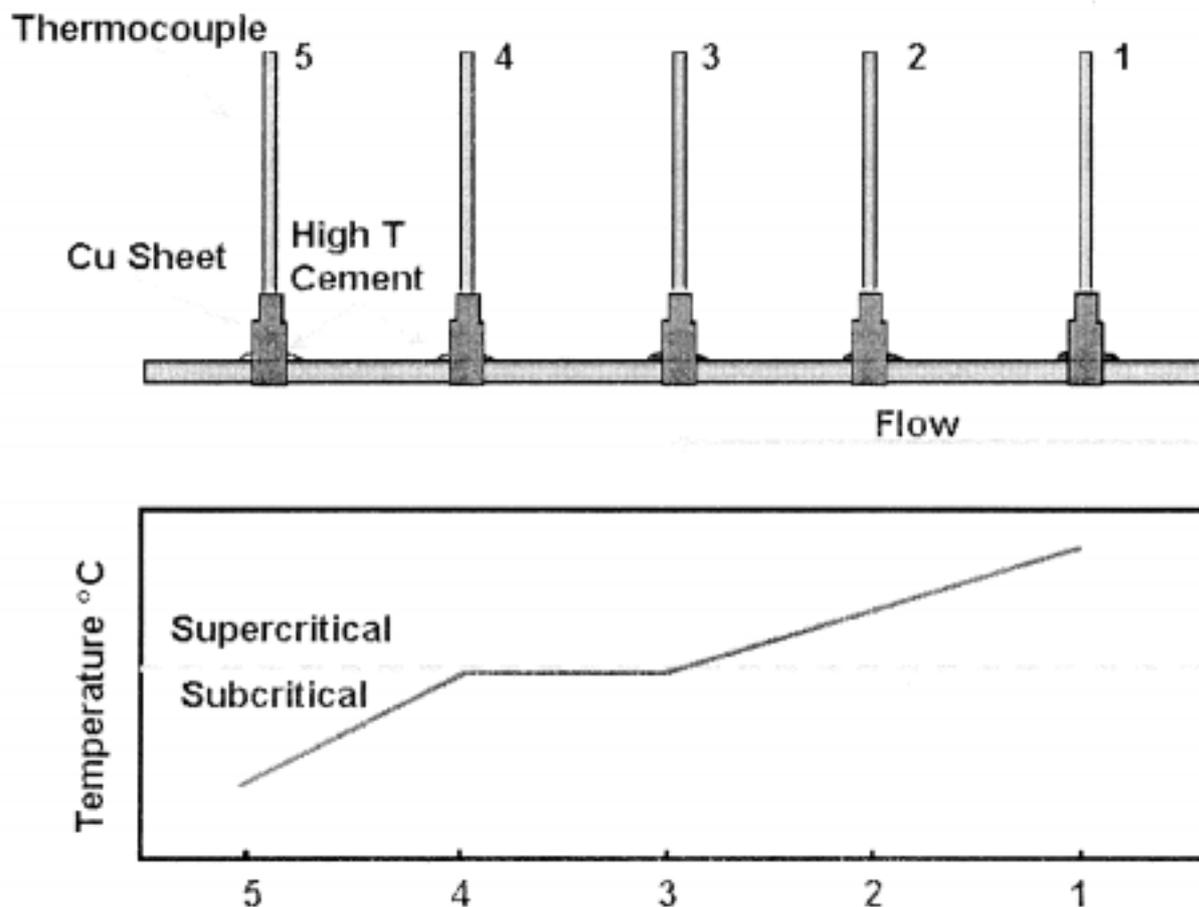


Fig. 5 : The instrumented tube setup developed at MIT.

higher pH values ($\text{pH} > 12$). When exposed to a highly chlorinated organic feed stream (0.3 wt% chloride) at 873K, weight loss data indicate a corrosion rate on the order of 50 mmpy and SCC for both stressed (U-bend) and non-stresses 316L samples. Ferralium 255 revealed a much lower corrosion rate (18 mmpy); however, degradation was anisotropic and more pronounced in the ferrite phase. When tested in chlorinated acidic conditions, a new Cr-Fe alloy, Ducrolloy (50%Cr, 44% Fe), apparently exhibited good corrosion resistance at exposure times up to 400 hours. While these data apparently agree with the general concept that corrosion resistance improves with increasing Cr content, results are preliminary and need to be confirmed by further testing.^{12,20,21}

6.2 Nickel-Base Alloys

There tends to be a more extensive database for this class of alloys than for others. This likely results as

high-nickel materials are frequently recommended for severe service applications and have, therefore, been utilized during fabrication for a number of bench-scale and pilot plant reactors. Notwithstanding this, the current database suggests that these materials may not be able to handle very aggressive SCWO feed streams as they might exhibit significant weight loss and/or localized effects including pitting, SCC and dealloying in aggressive environments. Dealloying is simply the preferential dissolution of one or more elements in an alloy due to the greater susceptibility of these elements to corrosion.

In DI water at elevated temperatures ($\sim 723\text{-}773\text{K}$), the general trend, even after extended exposure ($\sim 150\text{-}240$ h), is toward the formation of a potentially protective film for both Inconel 625 and Hastelloy C-276. Nevertheless, even for such innocuous conditions, both minor pit development and grain boundary carbide formation have been

observed for alloy Inconel 625. As early as 1990,²⁵ dealloying of Cr and Mo (Inconel 625) or Cr, Mo and W (alloy C-276) was recognized as a potential contributor to degradation within SCWO systems. Based on effluent analysis, results suggested loss of Cr for non-chlorinated feeds, while selective dissolution of the main alloying element, Ni, was apparent for chlorinated feeds.²⁶ Corroboration was subsequently provided by metallographic examination during analysis of a failed C-276 SCWO preheater tube, which, for acidic chlorinated conditions, revealed severe depletion of Ni.^{27,28} Interestingly, this analysis also indicated that the most severe corrosion was associated with a high subcritical temperature and that, at SC conditions, in the absence of salt precipitates corrosion may actually be minimal for alloys such as C-276.²⁹

There is some evidence for a correlation between Cr content and corrosion resistance for Ni alloys in SCWO systems.³⁰ Certainly the high Cr alloys such as G-30 (~30 wt% Cr) exhibit reasonable corrosion resistance. Recent research exposing G-30 to an acidic chlorinated feed with a maximum temperature of 623K indicated a corrosion rate of approximately 4 mmpy.³¹ It was concluded that this is too high to permit the use of G-30 as a reactor material; however, as presented in section 6.4, 4 mmpy is on the same order as rates found for Pt and its alloys, suggesting that G-30 should not yet be omitted from testing.

Figure 6 summarizes corrosion rate data for different iron- and nickel-base alloys exposed to a TrimSol feed for 66.2 hours at 873K. TrimSol is a cutting fluid of proprietary composition used in nuclear applications; it contains chlorides and other aggressive species at high concentrations.

6.3 Titanium-Base Alloys

Preliminary tests on Ti indicated poor resistance to the non-chlorinated acidic feeds; however, resistance to the chlorinated feed was found to be acceptable. When exposed to chlorinated feeds, Ti grade 2 apparently exhibits a corrosion rate of less than 3.5 mmpy. Reportedly, Ti provides outstanding performance at subcritical and is as resistant as the Ni alloys at SC temperatures. In addition, good performance (grades 9 and 12) is observed during exposure to sludge. Although one group has suggested

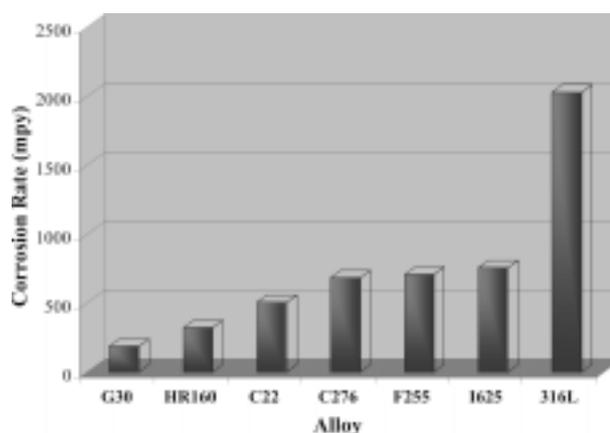


Fig. 6 : Corrosion rate data for samples exposed to a TrimSol feed for 66.2 hours at 873K.

Ti liners as a potential solution to corrosion problems in chlorinated organic feed streams, further testing is clearly required before a definitive answer will be found regarding the applicability of Ti-base alloys to these systems.^{12,20,21}

6.4 Noble Metals and Alloys

The use of noble metals or their alloys would significantly increase the initial cost of system fabrication. Nevertheless, for some very aggressive waste streams, they have been viewed as a possible solution to severe corrosion problems. An experiment carried out in a non-neutralized chlorinated feed stream with low level additions of Zn, Pb and Ce to assess materials suitability for SCWO included Pt and two Pt alloys (Pt-10Ir and Pt-30Rh).³² These materials were exposed for periods between 60 and 240 hours at two temperatures (673K and 883K). At the higher temperature all three materials revealed excellent corrosion resistance with rates on the order of 0.03-0.08 mmpy. At the lower temperature, however, corrosion rates for Pt, Pt-10Ir and Pt-30Rh were 1.14, 2.34 and 4.83 mmpy, respectively. While these rates may be acceptable for the normal engineering alloys, the high replacement cost associated with Pt or its alloys needs to be considered. Even at 1.14 mmpy, Pt losses could be on the order of hundreds of thousands of dollars a year. While the behavior of Pt is good at higher temperatures, in acidic chlorinated feeds it exhibits high rates of degradation at subcritical temperatures. For such feeds, this would necessitate a potentially troublesome transition between Pt and a second material.

6.5 Ceramics and Ceramic/Alloy Combinations

The problems associated with the corrosion of various alloys have prompted research into ceramic materials; however, results are not encouraging. With the possible exception of monolithic alumina and partially-stabilized zirconia (PSZ), ceramics have generally exhibited poor resistance to chlorinated waste streams over a wide pH (2-12) and temperature (623-773K) range. The general behavior for the ceramic materials tested (Al_2O_3 , AlN, Sapphire, Si_3N_4 , SiC and ZrO_2) in both chlorinated and non-chlorinated acidic feeds was found to be very poor. In aqueous sulfuric acid feeds, zirconia ceramics also exhibit poor resistance. Plasma sprayed multilayered ceramics on Ni or Ti substrates were exposed to a highly chlorinated feed and while none of the coatings was able to protect the Inconel 625 substrate, a titania multilayered ceramic system sprayed onto a titanium base showed promise.^{12,20,21}

7. POTENTIAL METHODOLOGIES FOR REDUCING CORROSION DAMAGE

Recognition of materials degradation as one of the central challenges to the ultimate commercialization of this technology has precipitated a number of potential methodologies for corrosion mitigation.

One potential methodology for reducing corrosion damage during the destruction of aggressive feeds would involve the use of a corrosion-resistant liner in conjunction with a pressure-bearing wall. Although some progress has been made in circumventing corrosion problems in this way, liners have not been extensively tested in these systems. In addition, the liner materials most frequently suggested for aggressive feed streams (titanium and platinum) tend to be expensive. Although the use of such a liner may be promising, as previously mentioned, there are conflicting reports on corrosion of the basic materials.^{12,20,21}

One possible alternative methodology would be to adjust the feed stream chemistry such that serious degradation is minimized. It may be possible to accomplish this by reducing the chloride concentration, or by altering the pH and oxidizing conditions such that the most favorable

thermodynamics are obtained.^{12,20,21}

Sufficient dilution of an aggressive feed can potentially reduce the risk of corrosion by lowering the chloride concentration and, thus, permit processing by SCWO. The required dilution may, however, be so large as to make such a procedure economically unattractive. For example, a dilution of 1,000-10,000 for wastes high in solvents such as carbon tetrachloride may be required to reduce feeds to acceptable levels.³³

8. CONCLUSIONS

The use of supercritical water either for destruction of hazardous waste or as the coolant in a direct-cycle nuclear reactor is of great interest. In both cases, corrosion of the constructional materials is of major concern. The extreme operating conditions in SCWO feeds require identification and/or development of constructional materials that are capable of withstanding very aggressive environments. Methodologies such as adjustment of the feed stream chemistry may be applied to form conditions where corrosion is less favorable.

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