An Overview of Corrosion Phenomena in SCWO Systems for Hazardous Waste Destruction

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There is a need to destroy both military and civilian hazardous waste and an urgency, mandated by public concern over traditional waste handling methodologies, to identify safe and efficient alternative technologies. One very effective process for the destruction of such waste is supercritical water oxidation (SCWO). By capitalizing on the properties of water above its critical point, (374°C and 221 atm for pure water), this technology provides rapid and complete oxidation with high destruction efficiencies at typical operating temperatures. Nevertheless, corrosion of the materials of fabrication is a serious concern and the practicality of SCWO may be limited by the ability to control corrosion. This paper reviews the literature on the degradation characteristics of a number of candidate materials of fabrication, including iron, nickel, and titanium-base alloys, ceramics, and noble metals. In addition, a number of potential methodologies for reducing corrosion damage in SCWO systems have been reviewed.

Key words: Supercritical water oxidation, high temperature corrosion, hazardous waste destruction, corrosion in SCWO systems.

Introduction

There is in excess of 23,000 tons of chemical agent stockpiled (characterized and stored in a controlled environment) at eight sites within the continental United States. The composition and nomenclature for a number of agents are presented in Table 1). While production was stopped in the late 1960's, some of this waste may have originated as long ago as the 1940's7). In addition to the stockpiled munitions, there exists a significant, but unknown, quantity of non-stockpiled waste that also needs to be considered for destruction7). This non-stockpiled waste (all chemical agent materials outside the stockpile) is a growing technical challenge due to the variety and circumstances in which it is found7,13,14). The Chemical Weapons Convention (CWC), which was signed by 130 countries (January 1993) seeks to eliminate chemical weapons and their production early in the new millennium1,13,14). In order to be able to accomplish this, a safe, efficient and economical waste disposal methodology needs to be identified. While a number of traditional destruction methodologies such as landfill or incineration do currently exist, they face significant public opposition1). For example, although incineration is widely employed to destroy waste, it has resulted in serious public concern as a consequence of stack emissions and other problems. Further, the economics of incineration requires a relatively high concentration of waste in the feed stream and the previous practice of permitting aqueous waste concentration by evaporation in open ponds prior to disposal is no longer acceptable. The clean-up of military and civilian hazardous waste is, nevertheless, gaining national importance9).

In addition to chemical agents, there is a need for the Department of the Environment (DOE) to address the clean up of in excess of 160,000 m² of mixed waste in its charge. While Supercritical Water Oxidation (SCWO) is demonstrably capable of destroying such wastes, many of the DOE wastes contain solvents or oils that are high in chlorine or other potentially corrosive precursors (e.g. fluorine, sulfur, tributyl phosphate). During destruction by SCWO, these can be oxidized to acidic products. In the case of chemical agents (Table 1), the oxidation of Sarin (GB) produces a mix of hydrofluoric and phosphoric acids; the oxidation of VX results in sulfuric and phosphoric acids; and finally, the oxidation of mustard agent (HD) produces hydrochloric and sulfuric acids7). Such acidic conditions may result in significant corrosion of the process unit and, in the context of the development of scaled-up systems8,9,10), corrosion may ultimately be the deciding factor in the commercial application of this technology.

Characteristics of Supercritical Water

Figure 1 presents a schematic representation of the change in the solubility of organics and inorganics as well as the fluid density in the region of the critical point. As the critical point is approached, the density of water changes rapidly as a function of changes in either temperature or pressure. In this regime, the density is intermediate between that of liquid water (1000 kg·m⁻³) and low pressure water vapor (<1 kg·m⁻³). Typically, at SCWO conditions, water density is approximately 100 kg·m⁻³ and, consequently, the properties of supercritical water are significantly different from liquid water at ambient conditions. The
Table 1 The composition and nomenclature for a number of chemical agents [1].

<table>
<thead>
<tr>
<th>Agent Acronym / Name</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>GB (Sarin)</td>
<td>Isopropyl methylphosphonofluoridate</td>
</tr>
<tr>
<td>VX</td>
<td>0-ethyl S-diolisopropyramino-methyl methylphosphonothiolate</td>
</tr>
<tr>
<td>HD (Mustard)</td>
<td>Bis-2-(chloroethyl) sulfide</td>
</tr>
<tr>
<td>GF</td>
<td>Cyclohexyl methylphosphonofluoridate</td>
</tr>
<tr>
<td>GD (Soman)</td>
<td>Pinacolylmethyl-phosphonofluoridate</td>
</tr>
<tr>
<td>GA (Tabun)</td>
<td>O-ethylidimethyl-amidophosphoryl cyanide</td>
</tr>
</tbody>
</table>

Fig. 1 A schematic representation of the change in (i) organic solubility, (ii) inorganic solubility, and (iii) density in the temperature region close to the critical point.

dielectric constant of water at 25 MPa drops from approximately 80 at room temperature to 2 at 450°C and the ionic dissociation constant decreases from $10^{-14}$ at room temperature to $10^{-23}$ at supercritical conditions. These changes result in supercritical water acting essentially as a non-polar dense gas with solvation properties approaching those of a low-polarity organic. Under these conditions, hydrocarbons generally exhibit high solubility in supercritical water and, conversely, the solubility of inorganic salts is very low. The solubility of NaCl, for example, drops from about 37 mass% at 300°C to only 120 ppm at 550°C. The combination of the solvation and physical properties make supercritical water an ideal medium for the oxidation of organics. When organic compounds and oxygen are dissolved in water above the critical point, kinetics are fast and the oxidation reaction proceeds rapidly to completion. While the products of hydrocarbon oxidation are CO$_2$ and H$_2$O, heteroatoms are converted to inorganic compounds (usually acids, salts or oxides in high oxidation states). As a result of the relatively low temperature of operation NO$_x$ and SO$_x$ are not produced.

The Process

Figure 2 presents a schematic diagram of a waste treatment system based on SCWO technology. In this process, aqueous organic waste (1), which may be neutralized with a caustic solution (2) or have fuel (3) injected for startup is initially pressurized from ambient to the pressure of the reaction vessel and pumped through a heat exchanger (4). This helps to bring the stream up to the desired temperature before reaching the reactor. At the head of the reactor (5), the stream is mixed with air or oxygen. In some cases, an oxidant such as hydrogen peroxide (H$_2$O$_2$) may be utilized in preference to either air or oxygen; however, this is not economically advantageous. The reaction occurs in the top zone (6), where spontaneous oxidation of the organics liberates heat and raises the temperature to levels as high as 650°C. Organic destruction occurs quickly with typical reactor residence times of one minute or less. As a result of their low solubility, salts precipitate and impinge on the lower zone (7), which is at a temperature of about 200°C. The salts may be continuously taken off as a brine (8) or removed periodically as solids. The primary effluent (9) passes out the top of the reactor into a separator (10) where the gas (11) and liquid (12) are quenched and separated. Finally, while a portion of the liquid remains in the system and is recycled (13) some is taken off as an effluent (14). Heat can be recovered from the treatment process stream and used to preheat the feed (4) or potentially to produce steam for electric power generation.

The Benefits of SCWO

Supercritical water oxidation is one potentially promising technology applicable to many organic wastes and has been shown to be well suited to handling dilute wastes in the range 1-20 mass%, which are not suitable for disposal by either incineration or landfill. High destruction efficiencies are possible for temperatures above approximately 550°C, even for short reactor residence times. An additional benefit is that, as a result of the relatively low operating temperature, NO$_x$ and SO$_x$ compounds are not
Corrosion Problems in SCWO Systems

Introduction

The major disadvantages of SCWO revolve around high pressure \((P > 23 \text{ MPa})\), potential solids handling problems, and, for some waste streams, corrosion\(^{11}\). Although SCWO is technologically able to destroy hazardous wastes, the process must be carried out in a reactor capable of accommodating elevated temperatures, pressures and, potentially, a very aggressive environment. The potential materials of fabrication covered within this section include: (i) Iron-Base Alloys, (ii) Nickel-Base Alloys, (iii) Ceramics and Ceramic/Alloy Combinations, (iv) Noble Metals and Alloys, and (v) Titanium-Base Alloys.

Iron-Base Alloys

In general, except for innocuous feed streams, alloys such as 316-L (Table 2) 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. Nevertheless, recent results suggest that a high chromium iron-base material (50 mass% Cr) may exhibit reasonable behavior even for an acidic chlorinated influent. Results are, however, of a preliminary nature and a significant amount of research would need to be done in order to confirm this trend.

Although selected feed streams may be innocuous enough to permit the use of AISI Type 316-L stainless steel, processing would need to be restricted to low halogen, moderate pH influents\(^{10}\). When exposed to deionized water within the temperature range 300–500°C, 316-L may reveal general corrosion and excellent overall performance\(^{15}\) or, alternatively, localized effects such as pitting\(^{16}\), intergranular corrosion (300°C) or crevice corrosion (500°C)\(^{17}\) may be seen.

Within a restricted pH range \((\approx 2-11)\) and for an influent with minimal Cl, 316-L may exhibit reasonable performance\(^{18}\) and a uniform corrosion rate as
Table 2  The nominal chemical composition of selected alloys (mass%).

<table>
<thead>
<tr>
<th>Alloys</th>
<th>625</th>
<th>276</th>
<th>C-22</th>
<th>HR-160</th>
<th>G30</th>
<th>316-L</th>
<th>F255</th>
<th>L-868</th>
<th>20CB3</th>
<th>2205</th>
<th>Ducrolloy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
<td>20.0-23.0</td>
<td>14.5-16.5</td>
<td>22</td>
<td>28</td>
<td>30</td>
<td>16-18</td>
<td>24-27</td>
<td>20.4</td>
<td>19.55</td>
<td>22.5</td>
<td>50.2</td>
</tr>
<tr>
<td>Mo</td>
<td>8.0-10.0</td>
<td>15-17</td>
<td>13</td>
<td>1.0max</td>
<td>5.5</td>
<td>2-3</td>
<td>2.4</td>
<td>16.42</td>
<td>2.13</td>
<td>3.3</td>
<td></td>
</tr>
<tr>
<td>W</td>
<td>-</td>
<td>3.0-4.5</td>
<td>3.0</td>
<td>1.0max</td>
<td>2.5</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>4.06</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co</td>
<td>1.0max</td>
<td>2.5max</td>
<td>2.5max</td>
<td>30</td>
<td>5max</td>
<td>-</td>
<td>-</td>
<td>0.1-0.25</td>
<td>0.18</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N</td>
<td>0.1max</td>
<td>0.01max</td>
<td>0.010max</td>
<td>0.05</td>
<td>0.03max</td>
<td>0.08</td>
<td>0.04</td>
<td>0.01</td>
<td>0.02</td>
<td>0.02</td>
<td></td>
</tr>
<tr>
<td>Nb</td>
<td>3.15-4.15</td>
<td>(plus Ta)</td>
<td>-</td>
<td>1.0max</td>
<td>1.5max</td>
<td>-</td>
<td>-</td>
<td>0.08</td>
<td>0.58</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>5.0max</td>
<td>4-7</td>
<td>3.0</td>
<td>3.5max</td>
<td>15.0</td>
<td>Bal.</td>
<td>Bal.</td>
<td>1.03</td>
<td>Bal.</td>
<td>Bal.</td>
<td>44</td>
</tr>
<tr>
<td>Ni</td>
<td>58min</td>
<td>57(as bal)</td>
<td>56(as bal)</td>
<td>37(as bal)</td>
<td>43(as bal)</td>
<td>10-14</td>
<td>4.5-6.5</td>
<td>57.42</td>
<td>33.55</td>
<td>5.70</td>
<td></td>
</tr>
<tr>
<td>Si</td>
<td>0.50max</td>
<td>0.08max</td>
<td>0.08max</td>
<td>2.75</td>
<td>1.0max</td>
<td>2.0</td>
<td>1.5</td>
<td>0.23</td>
<td>0.62</td>
<td>0.70</td>
<td></td>
</tr>
<tr>
<td>Mn</td>
<td>0.50max</td>
<td>1.0max</td>
<td>0.50max</td>
<td>0.5</td>
<td>1.5max</td>
<td>2.0</td>
<td>1.5</td>
<td>0.045</td>
<td>0.04</td>
<td>0.006</td>
<td>0.014</td>
</tr>
<tr>
<td>P</td>
<td>0.015max</td>
<td>0.04max</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.03</td>
<td>0.03</td>
<td>0.001</td>
<td>0.001</td>
<td>0.002</td>
<td></td>
</tr>
<tr>
<td>S</td>
<td>0.015max</td>
<td>0.03max</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>-</td>
<td>-</td>
<td>2max</td>
<td>-</td>
<td>1.5-2.5</td>
<td>0.01</td>
<td>0.04Ti</td>
<td>0.008Al</td>
<td>5Al</td>
<td>0.3Ti</td>
<td>0.5Y2O3</td>
</tr>
<tr>
<td>Others</td>
<td>0.4Almax</td>
<td>0.4Ti max</td>
<td>0.35Vmax</td>
<td>0.35Vmax</td>
<td>0.5Ti</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

Nickel-Base Alloys

There tends to be a more extensive data base for this class of alloy than for others. This likely results as high-nickel materials are frequently recommended for severe service applications\(^\text{18}\) and have, therefore, been utilized during fabrication for a number of bench-scale and pilot plant reactors. Notwithstanding this, the current data base suggests that these materials may not be able to handle very aggressive SCWO feed streams\(^{18,19,20,21,22}\) as they may exhibit both significant weight loss and/or localized effects including pitting, stress corrosion cracking (SCC) and dealloying in aggressive environments.

In deionized water, at elevated temperatures (\(\approx 450-500^\circ\text{C}\)) the general trend, even after extended exposure (\(\approx 150-240\) hours), is toward the formation of a potentially protective film for both alloy-625\(^{18,19}\) and C-276\(^{19}\). Nevertheless, even for such innocuous conditions, both minor pit development\(^{28}\) and grain boundary carbide formation\(^{32}\) have been observed for alloy 625.

As early as 1990\(^{29}\), dealloying of Cr and Mo (I-625) or Cr, Mo and W (C-276) was recognized as a potential contributor to degradation within SCWO systems. Based on effluent analysis, results suggested loss of chromium for non-chlorinated feeds, while selective dissolution of the main alloying element, Ni, was apparent for chlorinated feeds\(^{30}\). Corroboration was subsequently provided\(^{24,25}\) by metallographic examination during analysis of a failed C-276 SCWO preheater tube, which, for acidic chlorinated conditions, revealed severe depletion of Ni. Interestingly, this analysis also indicated that the most severe corrosion was associated with a high subcritical temperature\(^{33}\) and that, at supercritical conditions, in the absence of salt precipitates, corrosion may actually be minimal for alloys such as C-276\(^{34}\).
Recently the concentration of Ni, Cr and Mo in the effluent was experimentally determined at three ambient pH values: 1.3, 7.0 and 12.7 at a high subcritical maximum test temperature (T_{max} = 350°C) and tabulated in the literature. Figure 3 was derived from the tabulated data and presents the relative concentration of Ni, Cr and Mo in the effluent for an Inconel 625 reactor exposed to various feed pH values. The nominal amount of each of the three elements is indicated on the right-hand ordinate. For an acidic chlorinated feed (ambient pH 1.3), the nickel concentration in the effluent was determined to be appreciably higher than the nominal Ni value for the alloy. Conversely, the Cr and Mo effluent concentrations were both significantly lower than their respective nominal values. This suggests selective dissolution of Ni and the probability of conditions associated with the thermodynamic stability of Ni^{2+} and CrOOH. For a neutral chlorinated feed (ambient pH 7), the shift in pH from acidic to more neutral conditions resulted in a significant decrease in the relative concentration of Ni and an appreciable increase in Cr and Mo in the effluent, suggesting conditions favorable to selective Cr dissolution. A further increase in pH (ambient pH 12.7) results in data that again reveal selective dissolution of Cr.

At supercritical temperatures for an untreated acidic chlorinated feed, high-nickel alloys I-625, C-22 and I-686 apparently follow a general trend in which the corrosion rate decreases between 400 and 600°C; however, a significant increase was recorded above 600°C. Conversely, within the same temperature range, the corrosion rate of C-276 increased with increasing temperature. While one report suggests no apparent pattern in the location of localized corrosion for alloy 625, there is significant evidence to suggest that the potential for corrosion of Ni alloys exposed to SCWO conditions is more pronounced in the high subcritical regime and that the aggressiveness of the solution may decrease above the critical point. Care is, however, necessary in extrapolating such behavior as cracking has also been reported at supercritical temperatures after extended exposure times.

In addition, to some extent, the upper temperature limit for severe corrosion depends on the pressure and, thus, density of the solution, with higher densities favoring corrosion. While an Inconel 625 tube exposed to an aqueous feed stream containing 1800 ppm HCl without the addition of oxygen, revealed only general corrosion a 10 fold increase in the concentration (18000 ppm) resulted in transgranular SCC within the subcritical temperature zone (300°C) after exposure for only 46 hours. Under more complex low pH conditions, others report both transgranular and intergranular cracking of I-625 at subcritical, but not at supercritical, temperatures. Hong has previously reported, however, observing SCC and pitting of I-625 exposed to a mixed methylene chloride isopropyl alcohol feed neutralized with NaOH after extended times at supercritical temperatures (300 hours at 580°C). In general, when tested in acidic chemical agent simulant feeds, corrosion of the nickel alloys (C-22, C-276, 625, 825 and HR-160) was unacceptably high for both chlorinated and non-chlorinated simulants. When exposed to a highly chlorinated feed at 600°C for a short duration (66.2 hours) HR-160 (30 mass% Co) exhibited reasonable performance based on weight loss data; however, in regions where the surface oxide layer was locally disrupted severe grain boundary corrosion was apparent. There is some evidence for a correlation between Cr content and corrosion resistance for Ni alloys in SCWO systems. Certainly the high Cr alloys such as G-30 (≈30 mass% Cr) exhibit reasonable corrosion resistance. Recent research exposing G-30 to an acidic chlorinated feed with a maximum temperature of 350°C indicates a corrosion rate of approximately 4 mmpy. The authors suggest this is too high to permit the use of G-30 as a reactor material; however, as presented in a subsequent section of this paper, 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.

Ceramics and Ceramic/Alloy Combinations

The problems associated with the corrosion of various alloys has prompted research into ceramic materials; however, results are not encouraging.

With the possible exception of monolithic alumina and PSZ (partially stabilized zirconia), ceramics have, generally, exhibited poor resistance to chlorinated waste streams over a wide pH (2–12) and temperature (350–500°C) 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 chemical agent simulant feeds was found to be very poor. In aqueous sulfuric acid feeds, zirconia ceramics also exhibit poor resistance.

![Figure 3: The change in the relative concentration of the main alloying elements in the effluent for a 1-625 sample exposed to feeds with different pH values (data after 32).](image-url)
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 alloy 625 substrate, a titania multilayered ceramic system sprayed onto a titanium base showed promise.

**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 platinum and two platinum alloys (Pt-10 Ir, Pt-30Rh). These materials were exposed for periods between 60 and 240 hours at two temperatures (400 and 610°C). 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, platinum 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 this case, this would necessitate a potentially troublesome transition between Pt and a second material. One experiment in which an Inconel-625 tube was coated with a 30 µm gold layer exhibited intergranular SCC and failed within 34 hours. Conversely, under the same conditions, the uncoated tube did not fail even after 150 hours. Such behavior suggests a potential danger in the use of noble liners. Loss of liner integrity could potentially lead to catastrophic failure as a result of enhanced and unexpected degradation of the pressure bearing wall.

**Titanium-Base Alloys**

Preliminary tests of Ti indicated poor resistance to the non-chlorinated acidic chemical agent simulant feeds; however, resistance to the chlorinated feed was found to be acceptable. When exposed to chlorinated feeds, titanium (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 supercritical temperatures. In addition, good performance (grades 9 and 12) is observed during exposure to sludge. One group has suggested titanium liners as the solution to corrosion problems in chlorinated organic feed streams. This suggestion would, however, appear to be premature as other researchers have experienced problems with titanium and report through-wall pitting of liners during destruction efficiency testing of a chlorinated waste. At elevated temperature, potential problems with creep also need to be considered for this material. Clearly, further testing is required before a definitive answer will be found regarding the applicability of titanium alloys to these systems.

**Potential Methodologies for Reducing Corrosion Damage**

A 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.

**Corrosion Resistant Liners and Coatings**

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 (titanium and platinum) most frequently suggested for aggressive feed streams tend to be expensive. Although the use of such a liner may be promising, as previously mentioned, there are conflicting reports on corrosion of basic materials.

**Feed Modification**

Although liners manufactured from materials such as platinum have been promoted as a solution to corrosion problems for some aggressive SCWO conditions, one possible alternative 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.

**Dilution** - 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 1000-10000 for wastes high in solvents such as carbon tetrachloride may be required to reduce feeds to acceptable levels.

**Neutralization** - Although feed neutralization, with NaOH for example, has seen some success in SCWO systems for acidic feeds, it has been carried out without a full understanding of its effect on corrosion.
Typically, feed neutralization involves stoichiometric quantities of neutralizer; however, there is evidence that a limited E-pH region exists where the stability of Ni, Cr, and Fe is thermodynamically favored for high subcritical conditions. Figure 4 presents the superimposed E-pH diagrams for Cr and Ni at 300°C. Position 1 in this figure has previously been associated with the potential and pH of an acidic chlorinated feed, and represents conditions that are stable for Cr but not stable for Ni. There is, thus, the potential for selective dissolution of Ni. The addition of a neutralizer to increase the pH to position 2 could alter conditions such that Ni would attain stability; however, Cr would become thermodynamically unstable, and selective dissolution of Cr could become active. While the addition of the incorrect quantity of neutralizer could result in the selective dissolution of either Ni or Cr for systems fabricated from alloys containing these elements, modifying the feed chemistry to position 3, where both Cr and Ni are thermodynamically stable, should minimize degradation. In order to accurately maintain optimum feed chemistry conditions, however, the use of in-situ potential and pH electrodes would be necessary.

Ultimately, as a comprehensive understanding is gained, it may be possible to employ feed chemistry control in conjunction with intelligent materials selection to reduce degradation to an acceptable level in SCWO systems handling aggressive influents.

**Reactor Design**

Over the years, a number of new or modified reactor designs have emerged. In general, such designs attempt to reduce exposure of the pressure bearing wall to the process fluid and to limit potential problems with plugging. In its simplest form, design modification has involved the use of a liner with deionized water between the vessel wall and the liner. More complex designs have included, the dual shell pressure balanced vessel (DSPBV), the transpiring wall reactor, and the reactor concept of a film-cooled hydrothermal burner (FCHB). In the latter case, while the authors were initially optimistic about the design, subsequent experiments revealed problems including corrosion of the core tube tip and coaxial tubes.

### Summary

During the Workshop on Corrosion in SCWO Systems held at MIT in 1993 the attendees recognized the potential for corrosion to restrict the commercialization of SCWO for aggressive waste streams. At that time, the group consensus was that a material of fabrication universally applicable to all sections of a SCWO system was extremely unlikely. As presented in this review, while the data base for the potential materials of fabrication for SCWO systems has increased significantly since then, the group consensus apparently still holds. The corrosion of the materials of fabrication remains a serious concern and a significant amount of research remains to be carried out to identify materials or methods to reduce degradation within all sections to an acceptable level.

### References


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