

saturation results, it is clear that the inferred retained austenite levels in the bearing balls are influenced by many variables, beyond simply length of service. Uncertainties in the design, manufacture, and deployment of such an engineering system can all affect the retained austenite level. The resulting variability in the magnetic saturation data precludes the construction of a fully deterministic relationship between retained austenite and length of service. By incorporating a probabilistic analysis, it may be possible to predict the effect of various uncertain variables on the ultimate transformation rate of retained austenite in such strategic accelerometers. This work, which is ongoing, would essentially allow description of an aging rate for the phase change aging mechanism.

Conclusions and Summary

Successful aging management ideally would encompass the following four phases:

- Detection: A part has a negative use/availability trend (Spares) or a performance parameter has systematically shifted (Performance).
- Diagnosis: Identify the source of shift (component, part, material) through engineering investigation (event tree, fault tree).
- Prediction: Establish an aging reference; collect material aging data; develop deterministic and probabilistic descriptions; solve model to predict age-related failure rates into the future (Analysis).
- Decision: Determine the most effective/economical approach considering remaining equipment service life and total predicted failures, with the following options: no action; repair/replace aging component as failures are detected; acquire new replacement components; or redesign components and retrofit.

Spares-basing has the advantage of thoroughness at the expense of the effort needed to obtain information on every part in the system. *Performance-basing* has the advantage that it lets the equipment itself identify when an aging issue is beginning to arise and needs attention, at the expense of requiring special tests and storage of enormous quantities of data. *Analysis-basing* has the advantage of being able to predict far into the future and to suggest what might happen if the system is deployed in an environment for which it had not been specifically designed, at the expense of intense scientific investigation and computation time. As illustrated by the case study of the strategic accelerometer, however, real-world equipment gerontology programs may require a mix of all three approaches to help manage aging equipment.

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An Overview of the Current Understanding of Corrosion in SCWO Systems for the Destruction of Hazardous Waste Products

D.B. Mitton, N. Eliaz, J.A. Cline, and R.M. Latanision

H.H. Uhlig Corrosion Laboratory,
Massachusetts Institute of Technology, U.S.A.

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

Address for Correspondence: Dr. D.B. Mitton, H.H. Uhlig Corrosion Laboratory, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Rm. 8-204, Cambridge, MA 02139, U.S.A. Tel: (617) 253-3313, Fax: (617) 253-8745, E-mail: bmitton@mit.edu

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.

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 [1]. While production was stopped in the late 1960's, some of this waste may have originated as long ago as the 1940's [2]. In addition to the stockpiled munitions, there exists a significant, but unknown, quantity of non-stockpiled waste that also needs to be considered for destruction [3]. This non-stockpiled waste (all chemical agent materials outside the stockpile [4]) is a growing technical challenge due to the variety and circumstances in which it is found [1, 3, 4]. 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 millennium [2, 5]. 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 opposition [6]. 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 importance [6].

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 m³ 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 acids [7]. Such acidic conditions may result in significant corrosion of the process unit and, in the context of the development of scaled-up systems [8-10], corrosion may ultimately be the

Agent Acronym / Name	Composition
GB (Sarin)	Isopropyl methylphosphonofluoridate
VX	O-ethyl S-diisopropylamino-methyl methylphosphonothiolate
HD (Mustard)	Bis-2-(chloroethyl)sulfide
GF	Cyclohexyl methylphosphonofluoridate
GD (Soman)	Pinacolylmethyl-phosphonofluoridate
GA (Tabun)	O-ethyl dimethyl-amidophosphorylcyanide

Table 1 The composition and nomenclature for a number of chemical agents [1].

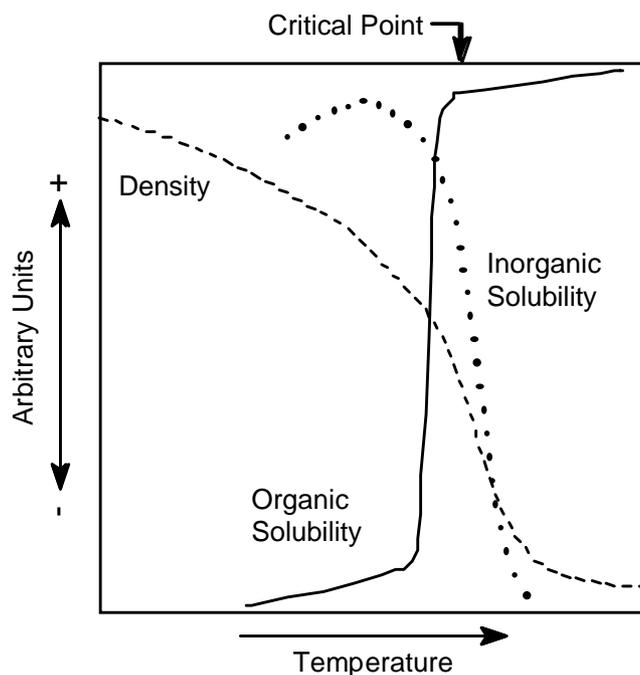


Figure 1 A schematic representation of the change in (i) organic solubility; (ii) inorganic solubility; and (iii) density, in the temperature region close to the critical point.

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 (1 g cm^{-3}) and low pressure water vapor ($<0.001 \text{ g cm}^{-3}$). Typically, at SCWO conditions, water density is approximately 0.1 g cm^{-3} and, consequently, the properties of supercritical water are significantly different from liquid water at ambient conditions. The 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 wt% 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_2O , 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_2 are not produced [11].

The Process

Figure 2 presents a schematic diagram of a down-flow vertical vessel waste treatment system based on SCWO technology [12]. 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_2O_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

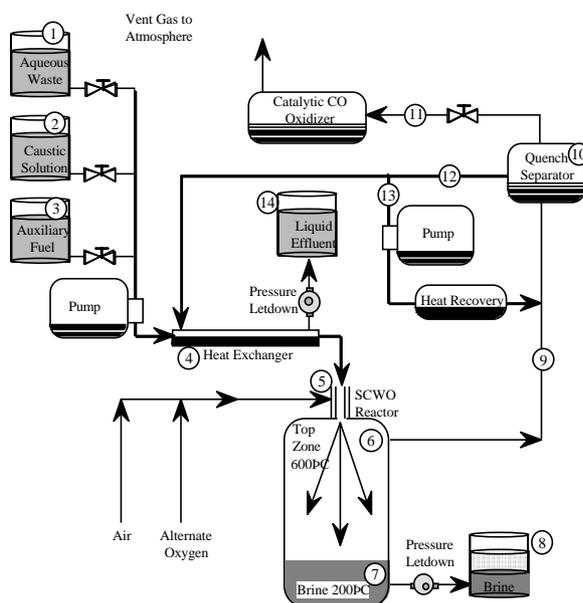


Figure 2 A schematic diagram of the SCWO process utilized by MODAR.

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 [11].

The Benefits of SCWO

Supercritical water oxidation is one potentially promising technology applicable to many organic wastes [11-13] and has been shown to be well suited to handling dilute wastes in the range 1-20%, which are not suitable for disposal by either incineration or landfill [6]. 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_2 compounds are not produced [11]. The latter may be particularly important during the destruction of explosives, which produce nitrogen oxides during incineration [14].

Alloys	625	276	C-22	HR-160	G30	316-
Cr	20.0-23.0	14.5-16.5	22.0	28.0	30.0	16.0-1
Mo	8.0-10.0	15.0-17.0	13.0	1.0 max	5.5	2.0-3
W	-	3.0-4.5	3.0	1.0 max	2.5	-
Co	1.0 max	2.5 max	2.5 max	30.0	5.0 max	-
N	-		-	-	-	-
C	0.1 max	0.01 max	0.010 max	0.05	0.03 max	0.08
Nb	3.15-4.15 (plus Ta)		-	1.0 max	1.5 max	-
Fe	5.0 max	4.0-7.0	3.0	3.5 max	15.0	Bal
Ni	58.0 min	57.0 (as bal)	56.0 (as bal)	37 (as bal)	43.0 (as bal)	10.0-1
Si	0.50 max	0.08 max	0.08 max	2.75	1.0 max	1.0
Mn	0.50 max	1.0 max	0.50 max	0.5	1.5 max	2.0
P	0.015 max	0.04 max	-	-	-	0.04
S	0.015 max	0.03 max	-	-	-	0.03
Cu	-	-	-	-	2.0 max	-
Others	0.4 Al max 0.4 Ti max	0.35 V max	0.35 V max	0.5 Ti	-	-

Table 2 - The nominal chemical composition of selected alloys.

Corrosion Problems in SCWO Systems

Introduction

The major disadvantages of SCWO revolve around high pressure ($P > 23$ 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 degradation behavior of various potential materials of fabrication is covered within this section.

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% 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 316-L stainless steel, processing would need to be restricted to low halogen, moderate pH influents

[15]. 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 ($\sim 2-11$) and for an influent with minimal Cl, 316-L may exhibit reasonable performance [15] and a uniform corrosion rate as low as 0.035 mmpy [16]; however, even for a restricted Cl feed, SCC may be observed at higher pH values ($\text{pH} > 12$) [15]. When exposed to a sludge, to a maximum test temperature of 425°C, 316-L exhibited pitting and crevice corrosion in both the subcritical and supercritical regions. For the same conditions, Alloy 20CB3 also displayed a high susceptibility to pitting, while Alloy 2205 reportedly exhibited good resistance except at attachment points, which revealed crevice corrosion [10]. When exposed to a highly chlorinated organic feed stream (0.3 wt% chloride) at 600°C, weight loss data indicate a corrosion rate on the order of 50 mmpy and SCC for both stressed (U-bend) and non-stressed 316-L samples. Ferralium 255 revealed a much lower corrosion rate (18 mmpy) [18]; however, degradation was anisotropic and more pronounced in the ferrite phase [19]. When tested in chlorinated acidic conditions a new Cr-Fe alloy, Ducrolloy (50% Cr, 44% Fe), apparently exhibited good corrosion resistance for exposure times up to 400 hours [20].

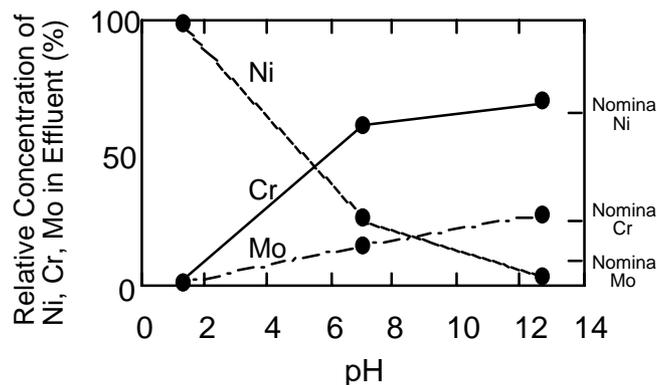


Figure 3 The change in the relative concentration of the main alloying elements in the effluent for an I-625 sample exposed to feeds with different pH values [data after 32].

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.

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 [21] 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 [7, 8, 15, 17, 22-27] 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 (~ 450 - 500°C), the general trend, even after extended exposure (~ 150 - 240 hours), is toward the formation of a potentially protective film for both alloy-625 [16, 17] and C-276 [17]. Nevertheless, even for such innocuous conditions, both minor pit development [17] and grain boundary carbide formation [28] 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

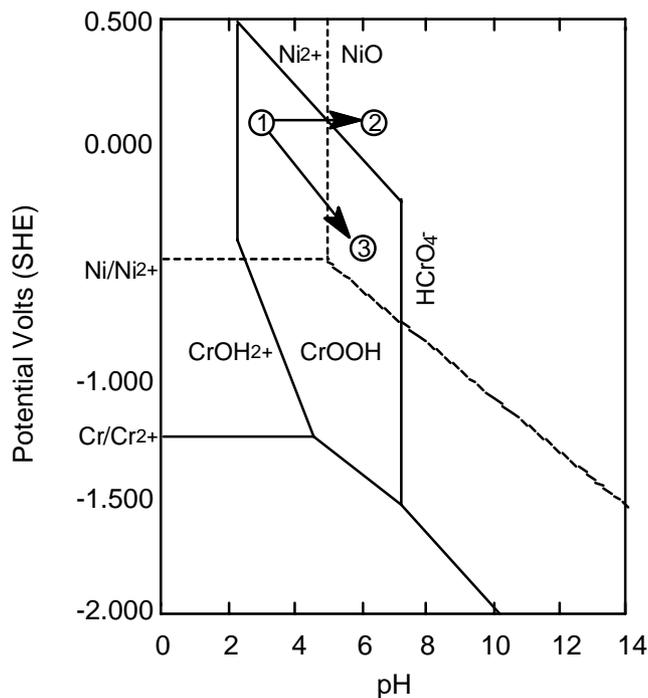


Figure 4 Superimposed E-pH diagrams for Cr and Ni revealing the region of selective dissolution for (1) Cr, or (2) Ni; and (3) the region of stability for both elements.

analysis also indicated that the most severe corrosion was associated with a high subcritical temperature [25] and that, at supercritical conditions, in the absence of salt precipitates, corrosion may actually be minimal for alloys such as C-276 [31].

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 ($T_{\text{max}} \sim 350^\circ\text{C}$) and tabulated in the literature [32]. 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 (Figure 4). 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 [33], 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 [23], 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 [24-26, 34] and that the aggressiveness of the solution may decrease above the critical point [35, 36]. Care is, however, necessary in extrapolating such behavior as cracking has also been reported at supercritical temperatures after extended exposure times [8]. 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 [34]. While an Inconel 625 tube exposed to an aqueous feed stream containing 1800 ppm HCl without the addition of oxygen, revealed only general corrosion [16], 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 [27] 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) [8]. 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 [7]. When exposed to a highly chlorinated feed at 600°C for a short duration (66.2 hours), HR-160 (30% 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 [19]. There is some evidence for a correlation between Cr content and corrosion resistance for Ni alloys in SCWO systems [37]. Certainly the high Cr alloys such as G-30 (~30% Cr) exhibit reasonable corrosion resistance [10, 19, 38]. Recent research exposing G-30 to an acidic chlorinated feed with a maximum temperature of 350°C indicated a corrosion rate of approximately 4 mmpy [20]. 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) [39], 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 [7]. In aqueous sulfuric acid feeds, zirconia ceramics also exhibit poor resistance [40]. 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 [37].

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-10Ir, Pt-30Rh) [33]. 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-10 Ir and Pt-30 Rh 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 acidic chlorinated feeds it exhibits high rates of degradation at subcritical temperatures [7]. For such feeds, this would necessitate a potentially troublesome transition between Pt and a second material.

Deposition of a thin gold layer on coupons during testing of various alloys and metals in a gold-lined vessel has been reported, and when exposed to a chlorinated acidified influent

gold was found to be unsuitable for use in SCWO reactors [41]. Experiments were, however, carried out in a static system and may, therefore, not be representative of conditions associated with a dynamic environment. An Inconel-625 tube 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 [16]. The latter 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 [7]. When exposed to chlorinated feeds, titanium (grade 2) apparently exhibits a corrosion rate of less than 3.5 mmpy [42]. Reportedly Ti provides outstanding performance at subcritical and is as resistant as the Ni alloys at supercritical temperatures [33]. In addition, good performance (grades 9 and 12) is observed during exposure to sludge [10].

More recently, Foy et. al. [43] reported on the oxidative hydrothermal destruction of chlorinated organics in a "corrosion-resistant" titanium-lined 316 stainless steel reactor. They monitored corrosion by analyzing for dissolved Ti

concentrations that were found to represent a uniform degradation rate on the order of 0.038-0.356 mmpy (1.5-14 mpy). From this, they conclude that titanium appears to be sufficiently protective; nevertheless, they recommend additional long-term testing. It is important to note that the majority of these experiments were carried out in a feed stream treated to achieve neutral pH. In addition, although they were unable to quantify the amount, the authors report observing, on several occasions, solid titanium (probably TiO_2) particulates filtered from the effluent. As the corrosion rate calculated by the authors is based on soluble Ti, and as the TiO_2 particulates indicate that not all titanium was soluble, the degradation rate would, of necessity, be higher than indicated. Further, although the corrosion rate calculation was based on the assumption that degradation was uniform, this was not established, and localized penetration rates would be significantly higher.

Others have experienced problems with titanium. Garcia [44] reported through-wall pitting of liners during destruction efficiency testing of a chlorinated waste. Another group reported Ti coupons were unaffected during expose to a static acidic chlorinated feed; however, a Ti autoclave suffered significant corrosion damage during similar tests on other metals and alloys. In some cases pitting as deep as 1 cm was reported [41]. Certainly, during exposure to the same environmental conditions, it is possible for titanium to exhibit substantially different corrosion behavior, depending on the presence or absence of occluded regions [45] and, to some extent, this may explain the apparently anomalous behavior of this material.

Although one group has suggested titanium liners as a potential solution to corrosion problems in chlorinated organic feed streams [46], further testing is, clearly, 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

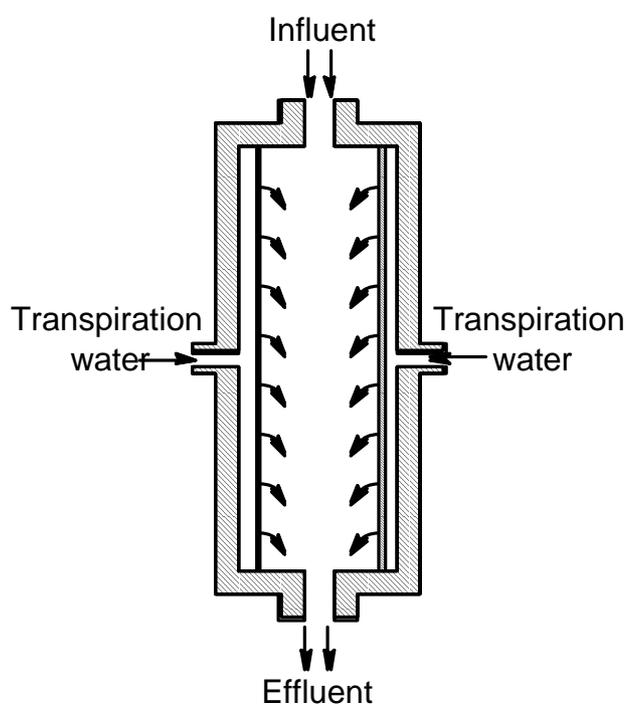


Figure 5 Schematic of a transpiring wall reactor.

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 [46] 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 [47].

Reactor design

The two main difficulties that must be overcome in SCWO systems are salt precipitation and corrosion. Over the years, in order, primarily, to deal with these problems, a number of reactor designs have emerged. In its simplest form, design

modification may involve the use of a liner with deionized water between the vessel wall and the liner [48]. More complex designs have included, the dual shell pressure balanced vessel (DSPBV) [49], and the reactor concept of a filmcooled coaxial hydrothermal burner (FCHB) [50]. 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 [51]. The most common designs involve (i) Down-flow vertical vessels (Figure 2), (ii) the tube configuration and (iii) the transpiring wall reactor [52]. The latter permits pure water to enter through apertures in the cylindrical reactor wall (Figure 5). This clean transpiration water maintains a boundary layer free of corrosive species or solids deposited on the inner reactor surface.

Atomistic calculations

A promising parallel area of study that will advance the current understanding of corrosion phenomena in SCWO systems involves the use of atomistic calculations. The primary constituent of passive films protecting stainless steels and other high-performance industrial alloys is Cr_2O_3 [53-55]. In the aggressive SCWO environment, corrosion initiation may result if the oxide is disrupted by species such as chlorides. While this phenomenon is well known, the associated atomic-level mechanisms are not fully understood [31, 56-57].

Experimentally, metal oxide surfaces are more difficult to study than pure metal surfaces [58]. Furthermore, as a result of the large number of valence electrons and the manifold of tightly bonded *d*-states, modeling of transition metal oxides using *ab initio* methods is computationally demanding [59]. Recently, advances in computer technology, in conjunction with the development of quantum-mechanical treatments such as density functional theory (DFT), have made such treatments of a metal oxide reasonable to perform. Overall, the density functional theory provides a computational method for determining the interactions of an oxide with other chemical species explicitly in terms of electronic states and bonding, allowing exploration of the responses of the multi-atom system to various mechanical and chemical stimuli [60].

An extended modeling effort to construct a rigorous and flexible model for Cr_2O_3 that will be useful for investigating localized chloride-assisted corrosion initiation and other surface chemistries, has been initiated at MIT. During this effort, a new neon-core pseudopotential for chromium was constructed by employing the methods of Rappe et al. [61]. This was then validated by calculating the electronic structure of bulk chromium metal under the local density approximation (LDA), and compared to calculations performed without a pseudopotential.

The chromium pseudopotential was then combined with

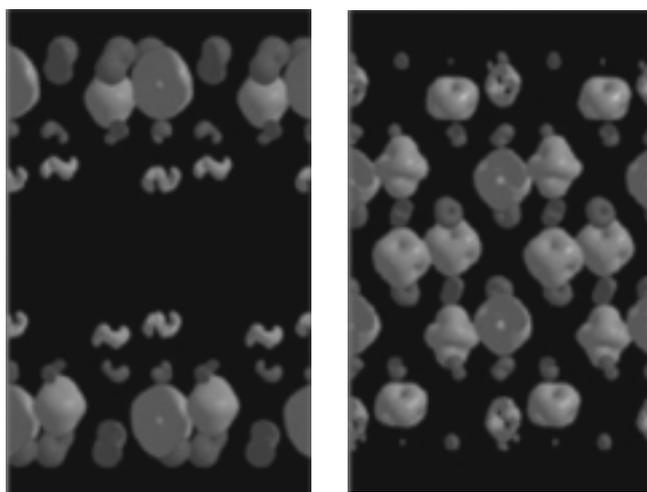


Figure 6 Local chemical softness map for a 28-atom surface slab of Cr_2O_3 . Portrayed are the HOMOs (a) and LUMOs (b) as calculated within LSDA. Figure shows a clear surplus of unoccupied states and deficit of occupied states at the surface, indicating chemical sensitivity to attack by electron-rich species. Chromium and oxygen atoms are shown in bright and dark colors, respectively [60].

a well-tested oxygen pseudopotential to compute *ab initio* the system of bulk Cr_2O_3 within the local spin-density approximation (LSDA) as well as the LDA under DFT. The LSDA calculations were found to describe the mechanical response, crystal asymmetries, thermodynamic and magnetic properties of Cr_2O_3 satisfactorily in comparison to experimental data and unrestricted Hartree-Fock calculations. The LDA results, when compared with the LSDA results, revealed that the effects of spin polarization in Cr_2O_3 help to define even basic properties such as bulk modulus [62].

With a validated first-principles model for the bulk crystal, a Cr_2O_3 slab was constructed for use in exploring surface chemistry. The oxygen-terminated (0001) surface of $\alpha\text{-Cr}_2\text{O}_3$ was computed under LSDA. Figure 6 presents the contour surfaces of the electron density of (a) the highest occupied molecular orbitals (HOMOs); and (b) the lowest unoccupied molecular orbitals (LUMOs) of the surface slab. These quantities represent the local chemical softness [63]. Figure 6 shows a remarkable spatial separation between the filled and empty states near the Fermi level. In particular, the chemical softness for the donation of electrons (represented by the LUMOs) is well localized on the surface, whereas chemical softness for acceptance of electrons is concentrated in the interior of the slab. Negatively charged species, such as chloride ions, coming in to contact with this surface will occupy spatial locations which accommodate their excess electrons with the lowest energy cost: the regions of high LUMO density. Such species would be expected to prefer the surface. Moreover, when sharing their electrons with these surface states, our results suggest that such species will preferentially disrupt the electronic structure of the surface. It should be noted that lowering the Fermi level, e.g. by p-type doping, may help transferring the new LUMOs to the interior, thereby protecting the surface [60].

Finally, a practical model should account not only for the changes in charge density and bonding at the oxide surface, but also for the changes in solvent properties that occur within SCWO process streams [64]. Therefore, the capability of computing the atomic-resolution effects of a dielectric upon the surface chemistry of Cr_2O_3 was developed in conjunction with the *ab initio* model. The bare Cr_2O_3 surface showed no significant changes in surface chemistry when a strong dielectric was present. Rough calculations of adsorption energies of chlorine onto the surface showed a dramatic decrease in energy in the presence of a dielectric. The dielectric is thus expected to have its strongest effect when the surface interacts with ions, creating strong dipoles which are geometrically accessible to the solvent [60].

This computational work has developed a tool which can be used to explore the surface chemistry of Cr_2O_3 , the main

constituent on passive films in common corrosion resistant alloys. This tool is now ready to be used to develop an *ab initio* density-functional description of the physical and chemical interactions between chlorine and Cr_2O_3 to explore mechanisms for chemical disruption of this passive film. Ideas for further development and application of this computational concept can be found in the work of Cline [60].

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 [8]. As presented in this review, while the database 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.

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