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Beyond the Aqueous Corrosion Paradigm: Solvent-Dependent Dissolution of Engineering Alloys in Non-Aqueous Acidic Halide Media

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Abstract

Corrosion behavior in non-aqueous acidic-halide environments remains poorly understood despite the widespread use of chlorinating reagents and chloride-containing species in pharmaceutical, agrochemical, and specialty chemical manufacturing. In the present study, we investigate the performance of engineering alloys in non-aqueous acidic-halide media using corrosion testing, inductively coupled plasma (ICP) analysis, electrochemical measurements, and flow-loop experiments.

Severe corrosion was observed during an industrial chlorination process performed in a C-22 reactor, a Ni-Cr-Mo-W alloy widely used in aggressive chemical service. Follow-up testing demonstrated that the phenomenon was not unique to C-22. Addition of acetonitrile (MeCN) increased the corrosion rates of corrosion-resistant Ni-alloys C-276 and C-2000 by approximately two orders of magnitude relative to analogous MeCN-free solutions, and similar susceptibility was observed across multiple engineering-alloy families. Alloy degradation occurred in environments containing chlorinating agents, including thionyl chloride ($SOCl_2$), sulfuryl chloride (SO_2Cl_2), and oxalyl chloride ($(COCl)_2$), as well as acidic chloride-containing species generated from hydrogen chloride and acidified chloride salts. ICP analysis detected substantial concentrations of major alloying elements, linking material degradation to process-stream contamination.

Corrosion testing, ICP analysis, and electrochemical measurements demonstrate that severe alloy degradation occurs when acidic chloride-containing species are combined with solvent environments that support continued alloy dissolution. Increasing water content progressively promoted passivation and suppressed dissolution, whereas flow dramatically accelerated attack, increasing the corrosion rate of C-276 in a 1 wt.% $SOCl_2$-MeCN solution from 12.1 to 540 mils

per year (mpy) (0.31 to 13.7 mm/y) at ambient temperature. These findings support a framework involving passive-film destabilization and solvent-dependent continuation of metal dissolution and offer new guidance for materials selection beyond the traditional aqueous paradigm.

Keywords: Non-aqueous corrosion, engineering alloys, acidic halide, chlorination, organic aqua regia, materials selection, passive film, acetonitrile, flow-assisted corrosion

Introduction

Acidic and halide-containing process streams are among the most corrosive environments encountered in chemical processing and dictate the selection of corrosion-resistant materials of construction[1]. Stainless steels, which are widely used in industry because of their relatively low cost and ease of fabrication, are generally unsuitable for aggressive acidic-halide service, necessitating the use of Ni-Cr-Mo alloys such as C-22, C-276, and C-2000. Although zirconium and tantalum may provide superior corrosion resistance in selected environments, their high cost, fabrication challenges, limited supplier availability, weldability constraints, and equipment-design considerations often limit their broader application, leaving Ni-based alloys as critical materials of construction for many process components[2]. The corrosion performance of these alloys in aqueous acidic-halide environments is relatively well-understood and forms the basis of materials-selection decisions[3-8].

Industrial chlorination processes, however, are frequently conducted in non-aqueous environments using chlorinating reagents such as thionyl chloride ($SOCl_2$), sulfuryl chloride (SO_2Cl_2), and oxalyl chloride $(COCl)_2$) in solvents including acetonitrile (MeCN),

dimethylformamide (DMF), tetrahydrofuran (THF), pyridine, and chlorinated hydrocarbons[9]. Many of these processes are operated under low-water conditions as water can hydrolyze chlorinating agents and reactive intermediates. However, low water content can create a trade-off between process performance and materials-of-construction corrosion resistance, as water generally promotes the formation and repair of protective passive film in corrosion-resistant engineering alloys[10,11]. Therefore, process conditions selected to minimize water content may simultaneously increase susceptibility to alloy degradation. This highlights a broader challenge in non-aqueous synthesis, where the conditions required for efficient chemical transformation may be incompatible with those needed to maintain alloy passivity.

Materials selection for chlorination processes extends beyond metals and alloys. Glass-lined steel is widely used in both aqueous and non-aqueous chlorination service because of its broad chemical compatibility. However, its application is often constrained by fabrication requirements, heat-transfer limitations, equipment design, mechanical service conditions, and inspection and repair considerations. Critical process equipment, including transfer piping, pumps, agitators, valves, heat exchangers, and dryers, frequently requires metallic construction. In addition to equipment degradation, corrosion of metallic components can introduce dissolved alloy constituents into process streams. The extent to which such corrosion contributes to process-stream contamination has received comparatively limited attention, despite its potential implications for product quality, downstream purification, and process performance. Therefore, corrosion-resistant engineering alloys remain essential materials of construction and are routinely exposed to aggressive chlorinating environments under both stagnant and flowing conditions.

The corrosion literature on materials performance in non-aqueous halide environments remains sparse compared with the extensive body of work on aqueous corrosion. Much of the foundational research examined pure metals, particularly Fe and Ni, in simplified organic electrolytes and demonstrated that solvent chemistry, acidity, halide species, and water content can profoundly influence dissolution and passivation behavior. These studies established important concepts of passivity in non-aqueous conditions but were not intended to predict the performance of commercial engineering alloys in industrial process environments[10].

Only a limited number of recent studies have directly examined corrosion-resistant engineering alloys in non-aqueous process chemistry. Schindelholz et al.[12] reported rapid dissolution of C-22 in an HCl-DDQ-MeCN pharmaceutical process solution and attributed the attack to oxidant-driven transpassive dissolution. Dick et al.[11, 13] subsequently demonstrated that acidity, chloride concentration, oxidizing species, solvent identity, and water content strongly influence the electrochemical behavior of C-22 in aprotic solvents. Separately, Wang et al.[14], working within an industrial pharmaceutical setting, reported corrosion of C-22 and C-276 in a Selectfluor-based process under low-water conditions. Together, these studies established that individual corrosion-resistant alloys can undergo severe degradation in selected non-aqueous environments, but they did not determine whether such behavior represents a broader materials-of-construction problem across commercial alloy systems and industrial chlorination chemistries.

A separate body of chemical research provides an important perspective on this problem. In work largely independent of the corrosion literature, Alfred A. Woolf demonstrated that SO_2Cl_2-MeCN reacts with a remarkably broad range of elemental metals under conditions where SO_2Cl_2 alone exhibits little reactivity and that metal dissolution depends strongly on

solvent[15]. These observations showed that the solvent can fundamentally alter metal reactivity rather than merely serving as an inert medium. More recently, the development of organic aqua regia (OAR) and related metal-dissolution systems demonstrated that combinations of chlorinating agents and selected organic components can efficiently dissolve noble and elemental metals under mild conditions. In these systems, the solvent plays an active role in promoting oxidative dissolution through coordination, complexation, and stabilization of dissolved metal species[16-18].

Despite recent advances, understanding of corrosion in non-aqueous chlorinating environments remains limited. Fundamental studies of non-aqueous corrosion established mechanisms of passivity and metal dissolution using pure metals and model organic electrolytes, whereas investigations of engineering alloys have largely been restricted to a small number of corrosion-resistant Ni-Cr-Mo alloys under specific process conditions. Thus, it remains unclear whether the severe corrosion reported in non-aqueous chlorinating systems represents isolated alloy-specific behavior or the manifestation of a broader degradation phenomenon controlled by coupled effects of passive-film breakdown and solvent-enabled metal dissolution. This distinction is important because conventional materials-selection approaches are largely based on aqueous corrosion concepts that emphasize passive-film stability but do not explicitly account for solvent-mediated stabilization of dissolved metal species. Furthermore, despite the widespread use of pumps, agitators, recirculation systems, and transfer lines in industrial chlorination processes, the influence of flow on corrosion in these environments remains largely unexplored. As a result, the combined effects of alloy composition, chlorinating-agent chemistry, solvent identity, water content, and hydrodynamic conditions on materials corrosion behavior remain poorly understood.

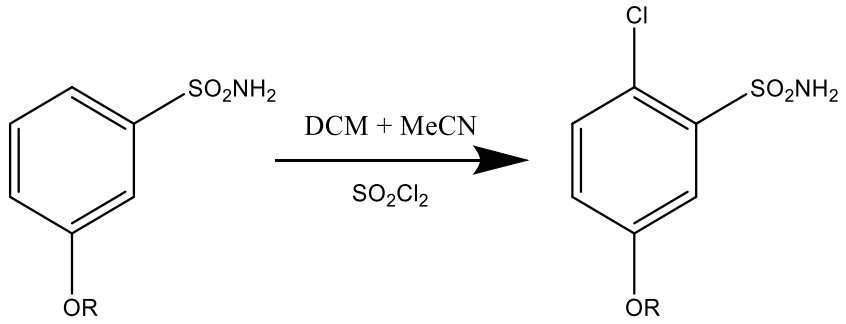
Based on observations of severe alloy degradation in an industrial chlorination process, it was hypothesized that rapid alloy degradation requires two concurrent conditions: (i) destabilization of protective passive films by acidic chloride-containing species, and (ii) an organic environment capable of sustaining dissolution and stabilization of released metal ions once passivity is lost. Increasing water content was expected to promote passivation and repassivation, whereas flow was expected to accelerate corrosion by influencing mass transport and corrosion-product removal. These hypotheses were evaluated using weight-loss measurements, inductively coupled plasma optical emission spectroscopy (ICP-OES) analysis, electrochemical testing, and flow-loop experiments across a broad range of alloys and process conditions. The study provides a unified framework linking alloy composition, chlorinating-agent chemistry, solvent environment, water content, and flow conditions, while offering practical guidance for materials selection in industrial chlorination processes and related non-aqueous chemical processes.

Results

High Corrosion Rate of Engineering Alloys in Non-Aqueous Halide Solutions Containing Acetonitrile

A chlorination reaction used in the manufacture of an agrochemical intermediate was conducted in a C-22 reactor at 80 ^{0}C and 370 psi. The reaction involved conversion of 4-alkoxybenzenesulfonamide to 2-chloro-4-alkoxybenzenesulfonamide, as shown in Scheme 1. The reactor was fabricated from alloy C-22, a Ni-Cr-Mo-W alloy commonly selected for severe chemical service because of its high resistance to aqueous acidic-halide environments.

After approximately 24 h of exposure, visible corrosion attack was observed on the reactor internal surfaces and agitator (Figure 1). ICP-OES analysis of the process solution detected several thousand ppm of dissolved Ni, Cr, Mo, W, and Fe. The dissolved-metal concentrations broadly reflected the alloy composition and did not indicate preferential dissolution of a specific alloying element. Notably, none of the individual reaction chemicals were known to be corrosive toward C-22 under comparable conditions.



4-alkoxybenzenesulfonamide 2-chloro-4-alkoxybenzenesulfonamide

Scheme 1: Chlorination reaction performed in a C-22 reactor.

The corrosion resistance of Ni-Cr-Mo and Ni-Cr-Mo-W alloys in aqueous acidic-halide environments is strongly influenced by Mo content[3]. Therefore, alloys with different Mo contents were initially expected to exhibit different corrosion behavior under non-aqueous conditions. Coupon testing was performed on C-276 (a Ni-Cr-Mo-W alloy) and C-2000 (a Ni-Cr-Mo-Cu alloy) in:

(a) 2.5% 4-alkoxybenzenesulfonamide, 4 equivalents of sulfuryl chloride (SO_2Cl_2), 18 wt.% acetonitrile (MeCN), and balance dichloromethane (DCM); and

(b) 2.1% 4-alkoxybenzenesulfonamide, 4 equivalents of SO_2Cl_2 and balance DCM, without MeCN.

Corrosion rates were determined from mass-loss measurements following the general guidance of ASTM G31[19]. In the MeCN-containing solution, the corrosion rates of C-276 and C-2000 were 144 mpy (mils per year) (3.66 mm/y) and 193 mpy (4.90 mm/y), respectively. In the corresponding solution without MeCN, the corrosion rates were 1.6 mpy (0.041 mm/y) for C-276 and 1.9 mpy (0.048 mm/y) for C-2000. The coupon data demonstrated that the addition of MeCN increased the corrosion rates by approximately 100 times for both C-276 and C-2000 alloys. Figure 2 shows the macrographs of as-welded coupons of C-276 and C-2000 alloys to process solution (a) and (b). In the presence of MeCN, there was a substantial uniform corrosion attack on both the tested alloys.

To determine whether extensive corrosion was limited to Ni-Cr-Mo alloys (C-22, C-276, C-2000), additional tests were performed on 316L stainless steel (a Fe-Cr-Ni-Mo alloy), alloy 400 (a Ni-Cu alloy), alloy 600 (a Ni-Cr-Fe alloy), alloy C-276, alloy C-2000, and alloy B-3 (a Ni-Mo alloy). The alloys were exposed to SO_2Cl_2 in DCM and to SO_2Cl_2 in a DCM-MeCN solvent mixture at 20 ^{0}C and 80 ^{0}C. The DCM:MeCN ratio was 4:1 (w/w).

As shown in Figure 3, all evaluated alloys exhibited substantially higher corrosion attack in the MeCN-containing solution than in the corresponding MeCN-free solution. Most tested alloys showed corrosion rates exceeding 100 mpy (2.54 mm/y), even at ambient temperature (20 ^{0}C). Furthermore, solution discoloration was observed during exposure and was consistent with alloy dissolution (Figure 4).

The measured corrosion rates contrast sharply with the established performance of these alloys in aggressive aqueous environments, where materials such as C-276, C-2000, and B-3 are routinely employed in hydrochloric acid, hydrofluoric acid, sulfuric acid, and mixed-acid service, often at elevated temperatures[2]. The increased corrosion rate associated with MeCN

was observed across Fe-Cr-Ni-Mo, Ni-Cu, Ni-Cr-Fe, Ni-Cr-Mo-W, Ni-Cr-Mo-Cu, and Ni-Mo alloy systems. The results demonstrate that corrosion behavior established in aqueous environments cannot be directly extrapolated to non-aqueous chlorinating media containing acetonitrile.

Role of Chlorinating and Chloride-Containing Chemicals in Acetonitrile-Induced Corrosion

The high corrosion rates observed in sulfuryl chloride-containing acetonitrile solutions prompted additional experiments to evaluate the influence of other chlorinating agents and chloride sources. Corrosion testing was performed on alloy C-276 in MeCN-containing thionyl chloride ($SOCl_2$), oxalyl chloride ($(COCl)_2$), N-chlorosuccinimide (NCS), and tetrabutylammonium chloride (TBAC) at ambient temperature. Although industrial chlorination processes typically employ significantly higher concentrations of chlorinating agents, lower concentrations were selected for corrosion screening purposes.

The corrosion-rate results are summarized in Table 1. Negligible corrosion was observed in MeCN, neat $SOCl_2$, and in a solution containing 10 wt.% $SOCl_2$ and water. In contrast, the addition of $SOCl_2$ to MeCN resulted in significant corrosion of alloy C-276. The corrosion rate increased from 12.4 mpy (0.32 mm/y) in 1 wt.% $SOCl_2$ + MeCN to 115.4 mpy (2.93 mm/y) in 10 wt.% $SOCl_2$ + MeCN.

Corrosion was also observed in solutions containing 1 wt.% $(COCl)_2$ and 1 wt.% N-chlorosuccinimide (NCS) in MeCN. However, the measured corrosion rates of 2.7 mpy (0.069 mm/y) and 1.2 mpy (0.030 mm/y), respectively, were considerably lower than those observed for $SOCl_2$-containing solutions.

To distinguish the effect of chlorinating agents from that of chloride-containing species, alloy C-276 was exposed to MeCN-containing 1 wt.% TBAC. No measurable corrosion was detected under these conditions. When 0.5 wt.% sulfuric acid (prepared from 98 wt.% reagent-grade H_2SO_4) was added to the TBAC-containing solution, C-276 coupon showed uniform corrosion. In contrast, no measurable corrosion was detected in a solution containing 10 wt.% H_2SO_4 in MeCN. These data demonstrate that acidity alone is insufficient to induce corrosion in acetonitrile and highlight the importance of chloride-containing species in enhancing alloy degradation. ICP analysis supported corrosion rate measurements. Elevated concentrations of dissolved Ni, Cr, Mo, W, and Fe were detected in solutions exhibiting measurable corrosion, whereas metal concentrations remained below the limit of quantification (LOQ) in non-corrosive solutions. Collectively, the results indicate that severe corrosion of C-276 in the environments investigated is associated with the simultaneous presence of acetonitrile, acidity, and chloride-containing species.

To further evaluate the role of acidic chloride-containing species, two separate experiments were performed. In the first experiment, anhydrous HCl was sparged into MeCN-containing C-276 specimens. In the second experiment, HCl was sparged into water containing identical specimens. ICP analysis of the solution containing MeCN detected 214 ppm Ni, 58.1 ppm Cr, 55.7 ppm Mo, 12.6 ppm W, and 24.8 ppm Fe, indicating substantial alloy dissolution. In contrast, all measured alloying elements remained below the LOQ in the aqueous HCl solution. The dissolved-metal composition broadly reflected the nominal composition of C-276, indicating largely congruent dissolution of the alloy. These results demonstrate that HCl can promote significant dissolution of C-276 in acetonitrile, whereas the corresponding aqueous environment did not produce measurable metal dissolution under the conditions investigated.

Another experiment was performed on a tantalum coupon in 10 wt.% $SOCl_2$-MeCN at ambient temperature. In contrast to C-276, which exhibited a corrosion rate of 115.4 mpy (2.93 mm/y) under the same conditions (Table 1), tantalum showed no measurable corrosion. Furthermore, ICP analysis detected no measurable tantalum dissolution, indicating exceptional resistance to the chlorinating-MeCN environment.

Role of Organic Solvents in Chloride-Induced Alloy Dissolution

The preceding results demonstrated that chlorinating agents and chloride-containing acidic species can promote corrosion of alloy C-276 in MeCN-containing environments. To determine whether this behavior was unique to MeCN or influenced more broadly by solvent chemistry, additional experiments were conducted using 1 wt.% $SOCl_2$ in a range of industrially relevant solvents, including tetrahydrofuran (THF), dimethylformamide (DMF), pyridine (Py), acetonitrile (MeCN), ethyl acetate (EtOAc), dichloromethane (DCM), and water. A concentration of 1 wt.% $SOCl_2$ was selected because it produced measurable corrosion while remaining sufficiently diluted to enable comparison of solvent effects on alloy dissolution. The solvents were selected to represent a range of chemical functionalities commonly encountered in chlorination processes, including ethers (THF), amides (DMF), nitrogen-containing bases (Py), nitriles (MeCN), esters (EtOAc), chlorinated solvents (DCM), and water.

Table 2 summarizes the concentrations of dissolved alloying elements measured by ICP following 8 d exposure of alloy C-276 to solutions containing 1 wt.% $SOCl_2$. The results reveal a strong dependence of alloy dissolution on solvents and distinguish three distinct solvent behaviors.

a. Solvents associated with measurable alloy dissolution (THF, DMF, Py, and MeCN):

Measurable concentrations of Ni, Cr, Mo, W, and Fe were detected in THF, DMF, pyridine, and MeCN. The presence of all major alloying elements in solutions indicates dissolution of alloy C-276 in these solvent environments. The dissolved-metal composition broadly reflected the nominal alloy composition, indicating largely congruent dissolution.

b. Solvents associated with negligible alloy dissolution (EtOAc and DCM):

In contrast, all measured alloying elements remained below the analytical LOQ in both ethyl acetate and dichloromethane. No measurable alloy dissolution was detected under the conditions investigated. This observation is noteworthy because the $SOCl_2$ concentration and exposure conditions were identical to those used in the solvents exhibiting measurable alloy dissolution.

c. Water:

Like ethyl acetate and dichloromethane, all measured alloying elements remained below the LOQ in water. Although no measurable metal dissolution was detected in either case, the behavior of water is considered separately because water helps in passivation/repassivation of alloy C-276, therefore, the low dissolved-metal concentrations in water are attributed to suppression of active dissolution through passivation rather than the mechanism operating in ethyl acetate or dichloromethane.

These results demonstrate that solvent identity exerts a significant influence on alloy dissolution in $SOCl_2$-containing media.

Effect of Water Concentration on Alloy Dissolution in Chlorinating Media

Table 3 summarizes representative dissolved-metal concentrations measured after 24 h exposure of C-276 spherical specimens in MeCN, $SOCl_2$, and 1 wt.% $SOCl_2$-MeCN solutions containing selected water concentrations. The complete water-concentration dataset is provided in Supplementary Table S1. Neither MeCN nor $SOCl_2$ resulted in any metal dissolution. In contrast, substantial concentrations of dissolved Ni, Cr, Mo, W, and Fe were detected in the 1 wt.% $SOCl_2$-MeCN solution, confirming significant alloy dissolution under these conditions.

Water concentration strongly influenced alloy dissolution. Measurable concentrations of Ni, Cr, Mo, W, and Fe were observed over a broad water-content range from 0 to 5 wt.%, indicating that significant metal dissolution persisted despite water addition. In contrast, all alloying elements were below the LOQ at 10 wt.% water, indicating suppression of measurable metal dissolution.

Further, to evaluate the influence of water on alloy passivation, cyclic potentiodynamic polarization experiments were performed at different water concentrations (Figure 5). In solutions containing 1 wt.% water, C-276 exhibited predominantly active dissolution. Increasing the water concentration to 10 wt.% resulted in the emergence of a passive region, although passive current densities remained relatively high compared with those observed at 50 wt.% water and in the aqueous solution. These results demonstrate a progressive enhancement in passivation with increasing water content.

To assess whether this effect was specific to thionyl chloride, polarization measurements were also performed in oxalyl chloride containing acetonitrile solutions (Supplementary Figure S1). Similar electrochemical behavior was observed for both chlorinating agents. At 1 wt.% water, the polarization curves exhibited predominantly active dissolution with no well-defined passive region. Increasing the water concentration to 50 wt.% produced a pronounced passive region in

both systems. At high water content, the polarization responses of the two chlorinating agents became nearly identical, indicating a similar influence of water on the passivation behavior of C-276.

Flow-assisted Corrosion in Chlorinating Solvent System

The preceding results demonstrated that water promotes passivation of C-276 and suppresses measurable alloy dissolution under stagnant exposure conditions. However, process equipment is commonly exposed to flowing fluids, which can disrupt the formation and stability of protective passive films and thereby increase corrosion susceptibility. To evaluate the influence of flow on corrosion behavior, corrosion testing was conducted under controlled recirculating conditions.

An internally designed flow-loop system used to evaluate the influence of flow on corrosion behavior is shown in Supplementary Figure S2. Bent and straight tubular coupons were installed in the recirculating loop. Corrosion testing was performed on C-276 in 1 wt.% $SOCl_2$ + water and 1 wt.% $SOCl_2$ + MeCN at ambient temperature and a flow velocity of 1.2 m/s, which represents the maximum flow rate attainable with the current setup.

The corrosion rates measured under stagnant and flowing conditions are summarized in Table 4. In 1 wt.% $SOCl_2$ + water, corrosion was negligible under stagnant conditions (<0.1 mpy (< 0.003 mm/y)) but increased to 7.8 mpy (0.2 mm/y) under flow, indicating that measurable corrosion occurred even in the aqueous environment in a flowing solution. In 1 wt.% $SOCl_2$ + MeCN, the corrosion rate increased from 12.1 mpy (0.31 mm/y) under stagnant conditions to 540 mpy (13.7 mm/y) under flowing conditions. Although flow increased corrosion in both aqueous and non-aqueous $SOCl_2$-containing solutions, the corrosion rate was very high in the

$SOCl_2$-MeCN system. The corrosion rate measured under flow in the $SOCl_2$-MeCN solution was approximately 45 times higher than that obtained under stagnant conditions.

Discussion

The corrosion damage observed in the C-22 reactor (Figure 1) and the high corrosion rates measured for multiple engineering alloys (Figures 2-4), even at ambient temperature, demonstrate that alloys routinely used in aggressive aqueous acidic-halide service can exhibit unexpectedly poor performance in non-aqueous chlorinating environments. The broad susceptibility observed across Fe-Cr-Ni-Mo, Ni-Cu, Ni-Cr-Fe, Ni-Cr-Mo-W, Ni-Cr-Mo-Cu, and Ni-Mo alloy systems (Figure 3) further indicates that the corrosion process is not controlled by the composition of a particular alloy and reflects the strong influence of the surrounding chemical environment on corrosion behavior.

The corrosion screening results provide insight into the conditions required for active dissolution. As shown in Table 1, neither MeCN, neat $SOCl_2$, nor H_2SO_4-MeCN solutions produced measurable corrosion, whereas significant corrosion was observed in MeCN-solutions containing $SOCl_2$, $(COCl)_2$, HCl, or acidified TBAC. Thus, under the conditions investigated, neither acidity nor the presence of chloride-containing species alone was sufficient to account for the observed degradation. Instead, substantial alloy dissolution occurred when acidic chloride-containing environments were combined with specific organic solvents.

The strong dependence of corrosion behavior on solvent identity further indicates that the solvent plays a more active role than simply serving as a reaction medium. As shown in Table 2, extensive dissolution of Ni, Cr, Mo, W, and Fe occurred in MeCN, DMF, THF, and pyridine,

whereas all alloying elements remained below the LOQ in DCM and EtOAc despite identical $SOCl_2$ concentrations and similar exposure conditions. An important observation is that measurable corrosion occurred at $SOCl_2$ concentrations as low as 1 wt.% (Table 1). Although chlorination processes frequently employ substantially higher chlorinating-agent concentrations, the results demonstrate that even relatively low concentrations of chlorinating agents can significantly influence alloy performance when combined with susceptible solvent environments.

The contrasting behavior between MeCN, DMF, THF, and pyridine and EtOAc and DCM suggests that passive-film destabilization alone is insufficient to produce extensive corrosion. Instead, sustained alloy dissolution appears to depend on the ability of the solvent environment to support continued dissolution following surface-film breakdown. This interpretation is consistent with observations from organic aqua regia (OAR) and related metal-dissolution systems, where solvents such as MeCN, DMF, and pyridine have been proposed to facilitate dissolution through coordination and stabilization of dissolved metal-containing species[16-18]. While the present results clearly demonstrate a strong solvent dependence, they do not establish the specific molecular features responsible for the contrasting behavior of MeCN, DMF, THF, and pyridine relative to EtOAc and DCM. Additional studies involving dissolved-metal speciation and solvent-metal interactions are required to identify the dominant solvent properties governing susceptibility in non-aqueous chlorinating environments.

An important consequence of the observed alloy dissolution is the introduction of substantial concentrations of alloying elements into process streams. ICP analysis detected hundreds of ppm of Ni, Cr, Mo, W, and Fe from coupon testing and several thousand ppm in the industrial process solution. These concentrations indicate significant metals leaching into the process

stream. In pharmaceutical, agrochemical, and specialty-chemical manufacturing, such contamination may affect product quality, downstream purification requirements, catalyst performance, or process economics even before equipment integrity becomes a primary concern. The ICP results therefore establish a direct link between corrosion behavior and process-stream contamination.

A plausible interpretation is that corrosion proceeds through two sequential steps. First, acidic chloride-containing species attack the alloy surface and disrupt the protective surface films that normally suppress dissolution. Second, once metal ions are generated at the alloy-solution interface, continued corrosion depends on the ability of the surrounding solvent to sustain those dissolved species. This behavior differs from that typically observed in aqueous environments, where protective film breakdown is often followed by repassivation. As a result, corrosion behavior established in aqueous systems cannot be assumed to translate directly to non-aqueous acidic chloride-containing environments.

A noteworthy exception to the behavior of conventional engineering alloys was tantalum, which exhibited no measurable corrosion in 10 wt.% $SOCl_2$-MeCN under stagnant exposure conditions. The excellent performance of tantalum is consistent with its long-standing use in highly aggressive chloride-containing environments, including hot hydrochloric-acid service[20] where conventional corrosion-resistant alloys often exhibit unacceptable corrosion rates. From a practical perspective, this observation is particularly relevant because tantalum is frequently used for repair and patching damaged glass-lined steel equipment. The tantalum results therefore support the continued use of glass-lined steel and tantalum-based corrosion barriers for reactors and other equipment where such materials are practical. However, many critical process components, including transfer piping, pumps, heat exchangers, agitators, valves, and

dryers, cannot be readily fabricated from glass-lined steel because of mechanical, fabrication, operational, or heat-transfer requirements. Consequently, understanding the performance limits of engineering alloys remains essential for safe and reliable operation of chlorination processes.

The water-doping studies provide further insight into the mechanism controlling corrosion. If corrosion were governed solely by the presence of unreacted $SOCl_2$, measurable dissolution would be expected to disappear once sufficient water was added to hydrolyze the chlorinating agent. However, Table 3 shows that significant concentrations of dissolved alloying elements persisted at water concentrations substantially exceeding the stoichiometric requirement for complete hydrolysis of 1 wt.% $SOCl_2$ (~0.15 wt.% H_2O). Measurable dissolution remained evident up to 5 wt.% water and was suppressed only at substantially higher water concentrations. These observations indicate that hydrolysis of $SOCl_2$ alone cannot account for the reduction in corrosion observed at elevated water contents, suggesting that water influences corrosion through an additional mechanism.

The electrochemical measurements shown in Figures 5 and Supplementary Figure S1 provide insight into the mechanism responsible for this behavior. Increasing water concentration produced a progressive transition from active dissolution to stable passivation, with lower passivation current densities. Similar trends were observed in both $SOCl_2$ and $(COCl)_2$-containing solutions, indicating a similar influence of water for the two chlorinating agents investigated. Collectively, the ICP and electrochemical results suggest that increasing water content promotes repassivation. As water concentration increases, formation and stabilization of protective oxide films become increasingly favorable, eventually suppressing measurable alloy dissolution despite the continued presence of chloride-containing species.

Flow introduces an additional factor that significantly alters corrosion severity. To the authors' knowledge, there is no published information regarding the performance of corrosion-resistant engineering alloys in flowing non-aqueous acidic-halide environments. Thus, the present results provide an important perspective on materials performance under conditions more representative of industrial operation than conventional stagnant immersion testing. The flow-loop experiments (Supplementary Figure S2) demonstrated that corrosion increased under flowing conditions in both aqueous and non-aqueous $SOCl_2$-containing environments, although the magnitude of the effect was substantially greater in the $SOCl_2$-MeCN system. The measurable increase in corrosion observed in the aqueous solution indicates that hydrodynamic conditions can influence the balance between dissolution and repassivation even when water promotes passive-film formation.

In the 1 wt.% $SOCl_2$-MeCN solution, the corrosion rate increased from 12.1 mpy (0.31 mm/y) in stagnant conditions to 540 mpy (13.7 mm/y) under flow (Table 4), representing an approximately 45-fold increase in corrosion rate at temperature as low as ambient. The observed behavior is consistent with flow altering the balance between dissolution and repassivation, potentially through changes in near-surface mass transport and removal of dissolved corrosion products. The significance of the flow results is amplified by the fact that the corrosion rate of approximately 14 mm/y was measured in MeCN-solution containing only 1 wt.% $SOCl_2$. For comparison, corrosion-resistant alloy process piping typically has wall thicknesses on the order of several millimeters, therefore, a uniform corrosion rate of 14 mm/y would be expected to result in rapid wall loss and an unacceptably short service life.

From an industrial perspective, the flow results are particularly significant because many process components exposed to chlorinating environments, including transfer piping, heat

exchangers, pumps, agitators, valves, and dryers, cannot be readily fabricated from glass-lined steel due to mechanical, thermal, fabrication, or heat-transfer requirements. Consequently, engineering alloys are frequently required in portions of the process where fluid flow is unavoidable. The extremely high corrosion rate measured in the 1 wt.% $SOCl_2$-MeCN solution under flowing conditions therefore highlights a critical materials-selection challenge for equipment that cannot rely on glass-lined construction.

Based on the collective evidence from Tables 1-4 and Figures 1-5, a mechanistic framework can be proposed. Corrosion initiates when acidic chloride-containing species attack and destabilize the protective surface films in engineering alloys that normally provide corrosion resistance. Subsequent alloy dissolution is sustained when the solvent environment can support continued metal dissolution following surface-film disruption. Water progressively inhibits this process by restoring and stabilizing the protective passive film, whereas flow shifts the balance toward continued active dissolution by limiting passive-film persistence. The interplay between surface-film destabilization, solvent-enabled metal dissolution, repassivation, and flow effects therefore governs the corrosion behavior of engineering alloys in non-aqueous chlorinating environments. This framework explains why alloys that routinely provide excellent performance in aggressive aqueous acidic-halide service can experience corrosion rates exceeding hundreds of mils per year (mpy) in non-aqueous chlorinating environments, even at ambient temperature and at chlorinating-agent concentrations as low as 1 wt.% $SOCl_2$. The dramatic acceleration observed under flowing conditions further demonstrates that corrosion assessments based solely on stagnant testing may substantially underestimate risk in industrial processes, particularly in acidic-halide systems.

The industrial relevance of these findings extends beyond the specific case study investigated here. The solvent screening further demonstrates that measurable alloy dissolution is not confined to a single solvent or solvent class. Measurable dissolution occurred in chemically distinct solvents spanning several functional groups, whereas other solvents under otherwise comparable conditions produced negligible dissolution, highlighting the broader relevance and strong solvent dependence of alloy dissolution in these non-aqueous environments. While detailed process information is often proprietary and therefore rarely available in published literature, the present results suggest that corrosion of metallic equipment in non-aqueous chlorinating environments may represent a broader materials-of-construction challenge in agrochemical, pharmaceutical, and specialty-chemical manufacturing.

The findings have two distinct industrial implications. First, alloy dissolution can introduce substantial concentrations of metallic constituents into the process stream, potentially affecting product quality or downstream processing before loss of equipment integrity becomes the primary concern. Second, corrosion rates measured under stagnant conditions may substantially underestimate material degradation under flow conditions encountered in pumps, recirculation loops, agitators, transfer lines, or heat exchangers.

Materials-selection programs for non-aqueous chlorination processes should therefore consider the combined effects of reagent chemistry, solvent identity, water content, and flow conditions rather than relying primarily on aqueous corrosion databases or the compatibility of individual reagents. Where metallic construction is required, stagnant immersion testing may need to be supplemented by testing that more closely represents the intended process environment.

Methods

Specimen and Solution Preparation

Corrosion testing was conducted using C-276 (UNS N10276), C-22 (UNS N06022), C-2000 (UNS N06200), B-3 (UNS N10675), Alloy 400 (UNS N04400), Alloy 600 (UNS N06600), 316L stainless steel (UNS S31603), and tantalum (UNS R05200). The nominal compositions of the Ni-based alloys and 316L stainless steel are provided in Supplementary Table S2.

For corrosion rate measurements, unwelded and autogenously welded flat coupons were procured from Metal Samples (USA). Prior to testing, specimens were cleaned with acetone and deionized water and air-dried. To investigate the effect of water content on corrosion behavior in $SOCl_2$-MeCN solutions, spherical C-276 specimens were obtained from McMaster-Carr (USA).

For electrochemical measurements, custom C-276 specimens were fabricated from alloy stock supplied by Metal Samples. A tapped hole was machined into each specimen to establish electrical contact through a cylindrical metal rod connected to the external circuit. The rod was enclosed within a glass sheath and sealed with a polytetrafluoroethylene (PTFE) gasket to prevent exposure to the test electrolyte. Prior to testing, specimens were ground to a 600-grit finish using silicon carbide abrasive paper, rinsed with deionized water and acetone, and air-dried. During electrochemical testing, approximately one-half of the specimen surface was exposed to the test solution. A platinum foil served as the counter electrode, and a saturated calomel electrode (SCE) was used as the reference electrode.

Acetonitrile (MeCN), dichloromethane (DCM), tetrahydrofuran (THF), dimethylformamide (DMF), pyridine (Py), ethyl acetate (EtOAc), thionyl chloride ($SOCl_2$), sulfuryl chloride (SO_2Cl_2), oxalyl chloride ($(COCl)_2$), anhydrous hydrogen chloride (HCl), sulfuric acid (98 wt.% H_2SO_4), and tetrabutylammonium chloride (TBAC) were obtained from commercial suppliers and used as received unless otherwise noted.

Immersion Technique

Corrosion tests were conducted in sealed glass vials with alloy specimens fully immersed in the test solutions. Mass loss measurements and corrosion-rate calculations were performed in accordance with the general guidance of ASTM G31[19] and ASTM G1[21]. Prior to exposure, specimens were cleaned with ethanol, air-dried, and weighed. Following exposure, specimens were rinsed with ethanol, air-dried, and reweighed to determine mass loss. Corrosion rates were calculated from the measured weight loss, exposed surface area, exposure time, and alloy density.

Electrochemical Technique

Electrochemical measurements were performed in $SOCl_2$-H_2O, $SOCl_2$-H_2O-MeCN, and $(COCl)_2$-H_2O-MeCN solutions using a conventional three-electrode electrochemical cell. Prior to polarization testing, the open-circuit potential (OCP) was monitored for 1 h to allow the system to approach a near steady-state condition. Linear polarization resistance (LPR) measurements were subsequently conducted with the general guidance of ASTM G59[22]. Polarization scans were performed from −20 to +20 mV relative to the corrosion potential (Ecorr) at a scan rate of 0.167 mV/s. Upon completion of the LPR measurement, OCP was monitored for 20 min to allow re-equilibration of the specimen surface.

Cyclic potentiodynamic polarization (CPP) experiments were conducted to evaluate passive-film stability and anodic dissolution behavior. The forward scan was initiated at Ecorr and continued anodically to +1100 mV above Ecorr at a scan rate of 0.167 mV/s. The scan direction was reversed when either the upper potential limit was reached or the current density exceeded 1 mA/cm^2. Reverse polarization continued until no evidence of positive hysteresis remained. All potentials reported in this work are referenced to the saturated calomel electrode (SCE).

Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES)

The extent of alloy dissolution was quantified by measuring dissolved metal concentrations in the test solutions using inductively coupled plasma optical emission spectroscopy (ICP-OES). Following exposure, aliquots of the test solutions were collected and digested in a mixture of nitric acid (HNO_3), hydrochloric acid (HCl), and deionized water using a Milestone UltraWAVE microwave digestion system equipped with quartz digestion vessels to ensure complete dissolution of dissolved and suspended metal species. The digested samples were analyzed using an Agilent 5110 ICP-OES instrument.

Calibration standards and quality control solutions were analyzed throughout each analytical sequence. Quality control checks performed before and after sample analysis indicated minimal instrumental drift, confirming measurement accuracy and stability. Concentrations of dissolved alloying elements were used to quantify alloy dissolution and complement corrosion-rate measurements obtained from gravimetric weight-loss testing. Element concentrations below approximately 2 ppm are reported as below the limit of quantification (LOQ).

Flow-Loop Corrosion Testing

Flow-loop experiments were conducted to investigate the influence of fluid flow on corrosion behavior. The test apparatus consisted of a 1 L jacketed borosilicate glass reactor (Chemglass Life Sciences, USA), a magnetic-drive centrifugal pump with an encapsulated impeller (March Pump BC-3CP-MD), and a non-metallic electronic flow meter. The flow path was constructed using high-density polyethylene (HDPE) tubing and polytetrafluoroethylene (PTFE) fittings and valves, while straight and bent metallic tubing sections served as corrosion test specimens. A bypass line enabled adjustment of flow through the metallic test sections.

The test solution was continuously recirculated through the flow loop at a flow rate of 1.1-1.3 gal/min using 3/8-in. tubing, corresponding to an average fluid velocity of approximately 1.2 m/s. The locations of the straight and bent specimens exposed under flowing conditions are shown in Supplementary Figure S2.

Data Availability

The data that supports the findings in this study is available upon a reasonable request.

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Competing Interests

The authors declare no competing interests.

Authors' Contribution

AM conceived and supervised the study, developed the overall scientific framework, designed the experimental program, analyzed and interpreted the data, and prepared the manuscript. AR conducted immersion testing, electrochemical measurements, ICP-related experimental work, and flow-loop experiments, and contributed to technical discussions. YK and JD identified and documented the industrial corrosion case study, performed preliminary corrosion screening experiments, and contributed to technical discussions during the early stages of the project. NB and NS contributed to data interpretation, chemistry-related discussions and manuscript review. All authors reviewed and approved the final manuscript.

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Figure Legends

Figure 1: Corrosion damage observed on the internal surfaces and agitator of a C-22 reactor after approximately 24 h of exposure during the chlorination reaction shown in Scheme 1.

Figure 2: Macro-images of as-welded C-276 and C-2000 coupons tested at 80 ^{0}C in a mixture of (a) 4-alkoxybenzenesulfonamide, sulfuryl chloride, acetonitrile and DCM, and (b) 4-alkoxybenzenesulfonamide, sulfuryl chloride and DCM. In a mixture containing MeCN, both C-276 and C-2000 showed substantial uniform corrosion attack. The emergence of the weld region on the polished welded coupon surfaces after exposure provided additional visual evidence of surface attack. In contrast, the weld region remained indistinguishable on coupons exposed to the MeCN-free solution, consistent with the substantially lower corrosion rates measured under these conditions.

Figure 3: Corrosion rates of engineering alloys exposed to SO_2Cl_2/DCM and SO_2Cl_2/DCM/MeCN solutions at 20 ^{0}C and 80 ^{0}C.

Figure 4: Images of 316L, C-276 and C-2000 coupons tested at 80 ^{0}C for 24 h in (a) SO_2Cl_2 and DCM, and (b) SO_2Cl_2, MeCN and DCM (DCM: MeCN – 4:1 (w/w)). Substantial coupon corrosion and pronounced solution discoloration were observed in the MeCN-containing solution.

Figure 5: Cyclic potentiodynamic polarization curves of C-276 in 1 wt.% $SOCl_2$-MeCN solutions containing varying water concentrations and in aqueous solution. Increasing water content promotes passive behavior.

Solutions	Corrosion Rate (mpy)
MeCN	< 0.1
$SOCl_2$	< 0.1
10% $SOCl_2$ + Water	< 0.1
10% $SOCl_2$ + MeCN	115.4
1% $SOCl_2$ + MeCN	12.4
1% $(COCl)_2$ + MeCN	2.7
1% NCS + MeCN	1.2
1% TBAC + MeCN	< 0.1
1% TBAC + 0.5% H_2SO_4[(a)] + MeCN	3.3
10% H_2SO_4[(a)] + MeCN	< 0.1

Table 1. Corrosion rate of C-276 in acetonitrile, acetonitrile containing chlorinating agents and chloride sources at ambient temperature.

[(a)] 98% reagent grade H_2SO_4.

Solvent	Ni (ppm)	Cr (ppm)	Mo (ppm)	W (ppm)	Fe (ppm)
THF	581	214	199	40	76
DMF	513	136	133	28	53
Py	505	143	139	30	52
MeCN	340	99	91	41	21
EtOAc	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
DCM	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
Water	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ

Table 2. Dissolved alloy constituent concentrations measured by ICP after 8 days exposure of C-276 to 1 wt.% $SOCl_2$ in various solvents at ambient temperature. LOQ refers to limit of quantification.

Solution	Ni (ppm)	Cr (ppm)	Mo (ppm)	W (ppm)	Fe (ppm)
MeCN	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
$SOCl_2$	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
1 wt.% $SOCl_2$ + MeCN	221	262	367	87	226
1 wt.% $SOCl_2$ + MeCN + 0.1 wt.% H_2O	181	221	323	78	180
1 wt.% $SOCl_2$ + MeCN + 0.2 wt.% H_2O	130	175	302	68	144
1 wt.% $SOCl_2$ + MeCN + 1 wt.% H_2O	133	277	272	64	138
1 wt.% $SOCl_2$ + MeCN + 5 wt.% H_2O	66	70	287	48	146
1 wt.% $SOCl_2$ + MeCN + 10 wt.% H_2O	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ

Table 3. Influence of water concentration on dissolved alloy constituent concentrations in 1 wt.% $SOCl_2$-MeCN solutions after 24 h exposure of alloy C-276 spherical specimens. Neat MeCN and $SOCl_2$ are included as reference conditions. LOQ refers to limit of quantification.

Solutions	Stagnant solution	Flowing solution
1% $SOCl_2$ + Water	< 0.1 mpy	7.8 mpy
1% $SOCl_2$ + MeCN	12.1 mpy	540 mpy

Table 4. Comparison of corrosion rates (in mpy) of C-276 in stagnant and flowing $SOCl_2$-containing solutions. Flow markedly increased corrosion, with the largest measured rate occurring in the $SOCl_2$-MeCN solution.

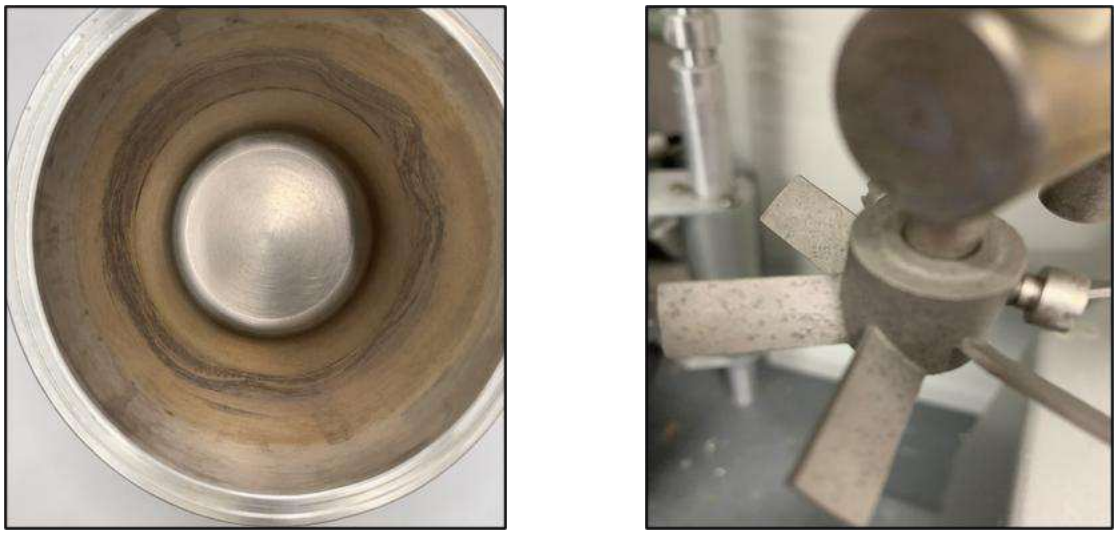


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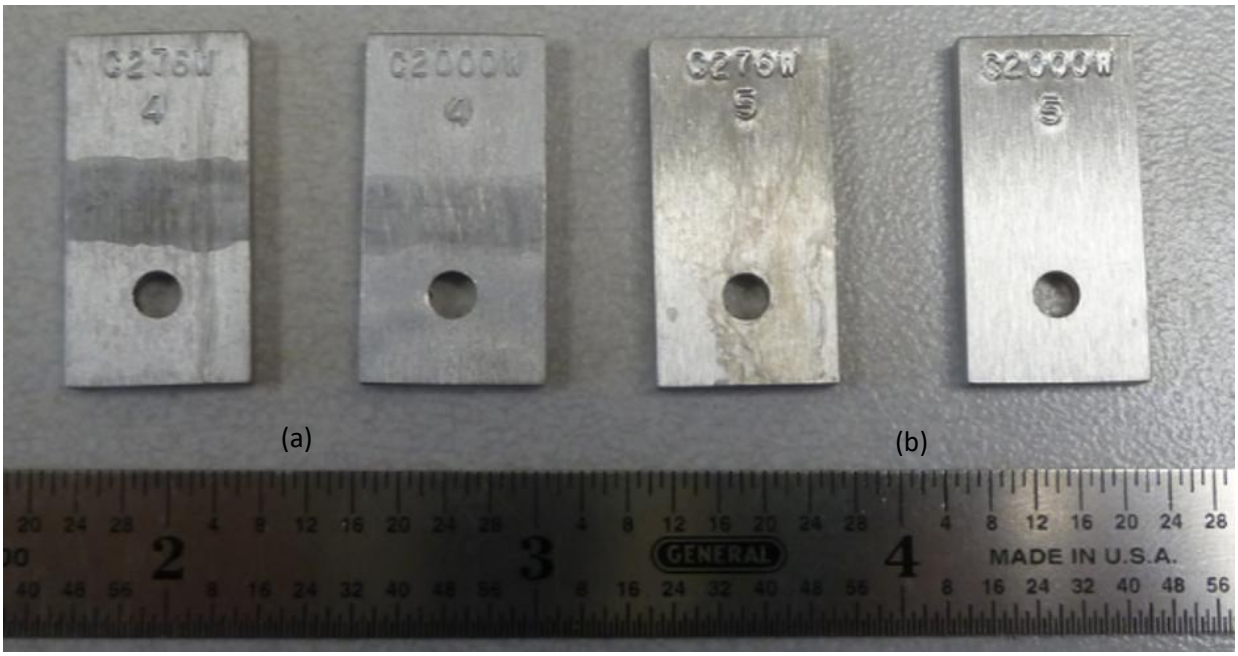


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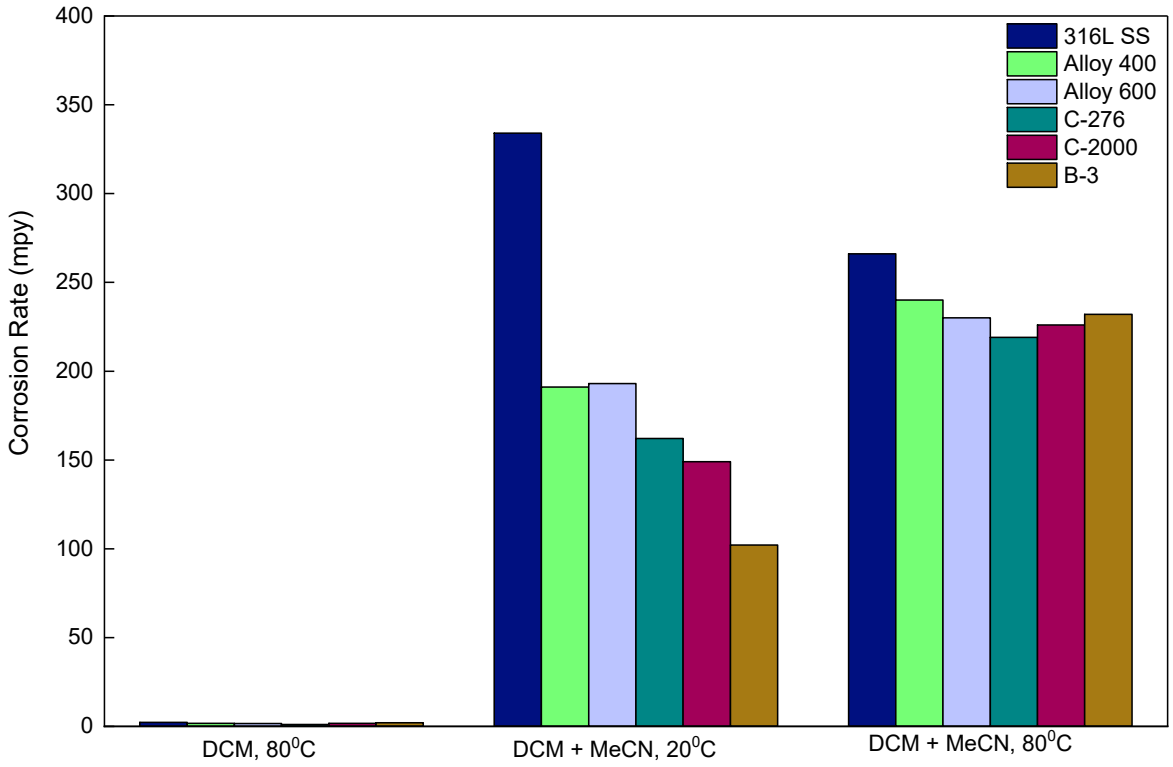
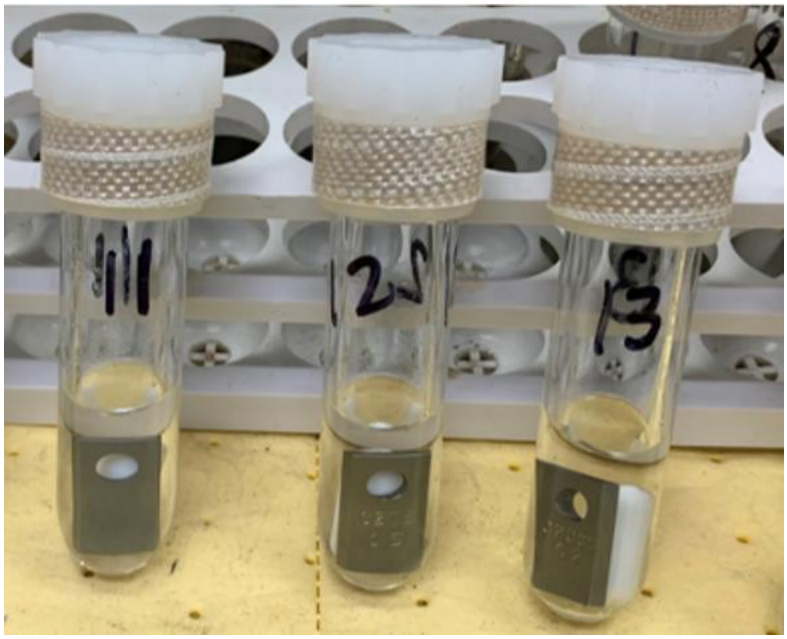
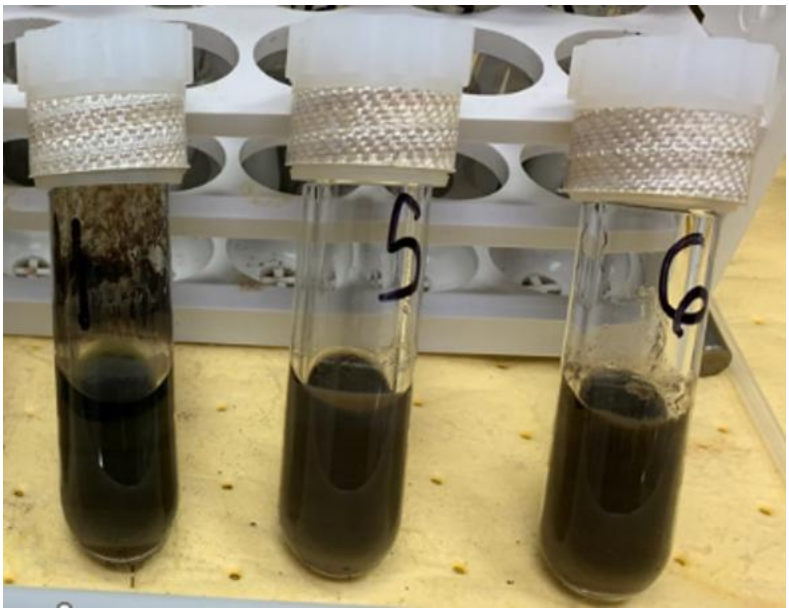


Figure 3. Corrosion rates of engineering alloys exposed to SO_2Cl_2/DCM and SO_2Cl_2/DCM/MeCN solutions at 20 ^{0}C and 80 ^{0}C.



(a)



(b)

Figure 4. Images of 316L (left), C-276 (center) and C-2000 (right) coupons tested at 80 ^{0}C for 24 h in (a) SO_2Cl_2 and DCM, and (b) SO_2Cl_2, MeCN and DCM (DCM: MeCN – 4:1 (w/w)). Substantial coupon corrosion and pronounced solution discoloration were observed in the MeCN-containing solution.

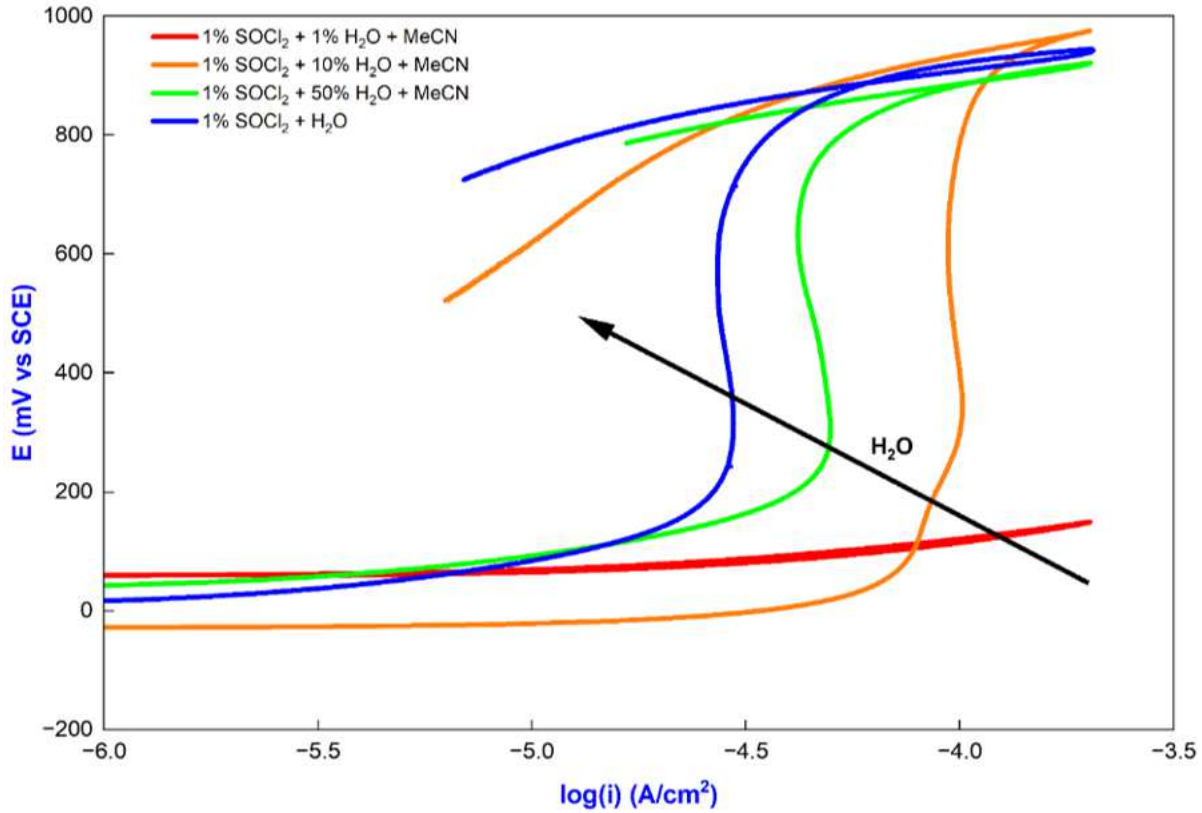


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