

# Inhibition of localized corrosion in chromium containing stainless alloys

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## Abstract

The application of stainless steels and chromium containing nickel-based alloys is limited by their susceptibility to localized corrosion in the forms of pitting and crevice corrosion or environmentally assisted cracking. Inhibitors may be normally found in service environments or added on purpose to mitigate or avoid the effects of aggressive agents such as chloride ions. The present study critically reviews the present knowledge on inhibition of chloride-induced pitting and crevice corrosion. Pioneering studies and recent findings are analyzed in light of the present theories for describing the localized corrosion processes. This review particularly focuses on the inhibition of crevice corrosion of alloy 22, which has been thoroughly studied in the past decade.

**Keywords:** crevice corrosion; inhibitor; nickel alloys; pitting corrosion; stainless steels.

## 1. Stainless alloys

Stainless steels and chromium containing nickel-based alloys are corrosion resistant materials that rely on the protection brought about by a passive overlayer (Agarwal, 2003; Rebak, 2000; Sedriks, 1996). This passive film is chromium-rich and it is spontaneously developed when the material is in contact with air or in the service environment (Marcus & Maurice, 2000). A certain minimum chromium content of the alloy is required for the passive film to be formed (Sedriks, 1996). Alloy passivation results from the formation of a continuous oxide or oxy-hydroxide layer on the alloy surface. This thin film protects the alloy against corrosion by isolating it from the corrosive environment (Marcus & Maurice, 2000).

The general corrosion rate of passive stainless alloys may be very low and it is not an issue for most practical applications. However, the passive film may locally break down in some environmental conditions leading to different forms of localized attack, namely pitting and crevice corrosion (Sedriks, 1996; Szklarska-Smialowska, 2005). These forms of corrosion generally occur, in practical applications, when passive metals

are exposed to near neutral or alkaline solutions containing an aggressive anion, usually chloride. Pitting corrosion is caused by local dissolution of passive metals leading to the formation of cavities. Crevice corrosion may occur within cracks and crevices where a stagnant solution is developed (Szklarska-Smialowska, 2005). Pitting corrosion and crevice corrosion are essentially the same phenomena from an electrochemical point of view, although there are geometrical differences between them (Galvele, 1976). Crevice corrosion is of particular concern for stainless steels and nickel alloys as it is possible in milder environmental conditions than those required for pitting corrosion (Agarwal, 2003; Rebak, 2000).

Localized corrosion inhibitors are species which are able to mitigate or avoid the occurrence of the localized attack. They may be normally found in service environments or added on purpose. The objective of the present study was to critically review recent findings regarding inhibitors of the chloride-induced localized corrosion of stainless alloys. Table 1 shows the chemical composition of the stainless alloys reviewed in this paper.

The effects of inhibitors on pitting and crevice corrosion are generally evaluated by measuring the critical potentials ( $E_{CRIT}$ ) or temperatures ( $T_{CRIT}$ ) associated with the alloys on localized corrosion occurrence. Localized corrosion occurs only above  $E_{CRIT}$  and  $T_{CRIT}$ . The critical potentials include those related to passivity breakdown, i.e., the initiation of pitting and crevice corrosion attacks ( $E_p$  and  $E_c$ , respectively), and also those related to the repassivation of pitting and crevice corrosion ( $E_{RP}$  and  $E_{RC}$ , respectively). Critical temperatures include the critical pitting and crevice temperatures (CPT and CCT, respectively).

## 2. Inhibitors and their efficiency

Early studies reveal that there is a critical ratio of inhibitive to aggressive anion concentration above which no pitting corrosion occurs (Leckie & Uhlig, 1966; Matsuda & Uhlig, 1964; Rozenfeld & Danilov, 1967; Schwenk, 1964; Sugimoto & Sawada, 1976). The relationship stated in Eq. (1) establishes the limit between pitting corrosion and its inhibition as a function of the concentrations of the aggressive and the inhibitive anions,  $C_A$  and  $C_I$ , respectively; where a and b are constants.

$$\log(C_A) = a + b \cdot \log(C_I) \quad (1)$$

$E_p$  has been reported to be a function of  $C_A$  and  $C_I$  according to Eq. (2), where c and d are constants, being d negative when  $C=C_A$  and d positive when  $C=C_I$  (Galvele, 1976; Leckie & Uhlig, 1966; Szklarska-Smialowska, 2005).

$$E_p = c + d \cdot \log(C) \quad (2)$$

**Table 1** Chemical composition (weight%) of stainless alloys reviewed in the present paper.

Alloy	Fe	Ni	Cr	Mo	N	C	Mn	Si	Others
304(UNS S30400)	Bal.	10	19	–	–	0.08	2.0	0.75	–
304L(UNS S30403)	Bal.	10	19	–	–	0.03	2.0	0.75	–
316(UNS S31600)	Bal.	10	17	2.5	–	0.08	2.0	0.75	–
316L(UNS S31603)	Bal.	10	17	2.5	–	0.03	2.0	0.75	–
316 Ti(UNS S31635)	Bal.	12	17	2.5	0.10	0.08	2.0	0.75	Ti 0.70
S318.03(UNS S31803)	Bal.	5.5	22	3	0.2	0.03	2.0	1.0	–
254SMO(UNS S31254)	Bal.	18	20	6.1	0.2	0.02	1.0	0.8	Cu 0.7
825(UNS N08825)	29	42	21.5	3	–	0.05	0.35	0.2	Cu 2.0
625(UNS N06625)	5	Bal.	21	9	–	0.1	0.5	0.5	Cb+Ta=3.7, Co 1.0, Ti 0.4, Al 0.4
22(UNS N06022)	3	Bal.	22	13	–	0.01	0.05	0.08	W 3.0

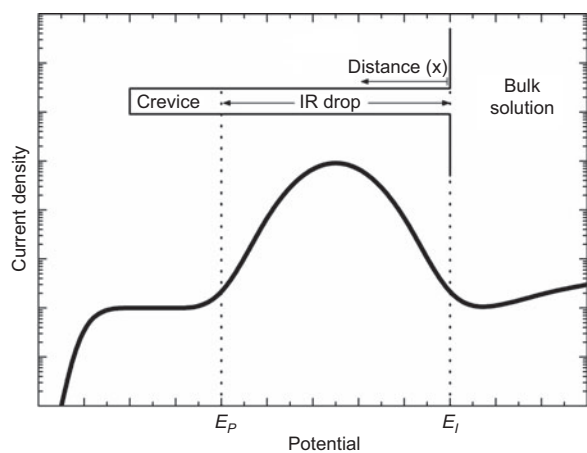
Pitting corrosion of metals is observed at potentials above  $E_p$ . However, in certain conditions, it may be limited to a definite range of potentials. The first pitting corrosion studies on stainless steels (SS) in chloride plus nitrate solutions indicate the existence of another characteristic potential called inhibition potential ( $E_i$ ) (Leckie & Uhlig, 1966; Schwenk, 1964). This potential also appears in other metal/electrolyte systems (Matsuda & Uhlig, 1964).  $E_i$  has little practical use, as in those regions where a high potential drop can be found, like in a crevice, the inhibition potential is not reached, and localized corrosion can proceed (Keitelman & Galvele, 1982). Figure 1 schematically shows a situation in which a creviced SS specimen is polarized at  $E_i$ . The ohmic drop (IR drop) causes the potential to be below  $E_i$  (and above  $E_p$ ) in a wide zone within the crevice.

It is well known that the presence of certain anions in sufficient concentration causes the increase of the  $E_{CRIT}$  or  $T_{CRIT}$  for stainless alloys in chloride solutions. The efficiency of different anions as pitting corrosion inhibitors of austenitic SS has been ranked by different authors. Leckie and Uhlig (1966) reported the following efficiency order  $\text{OH}^- > \text{NO}_3^- > \text{SO}_4^{2-} > \text{ClO}_4^-$ ; whereas Rozenfeld and Danilov (1967)

indicate a ranking for neutral solutions as follows  $\text{NO}_3^- > \text{ClO}_3^- > \text{ClO}_4^- > \text{CrO}_4^{2-} > \text{SO}_4^{2-}$ . However,  $\text{SO}_4^{2-}$  is more efficient than  $\text{CrO}_4^{2-}$  in acidic or alkaline solutions (Rozenfeld & Danilov, 1967). Solution pH plays an important role on the inhibition.  $E_p$  remains constant in the acid pH range, but it increases in the alkaline range (Leckie & Uhlig, 1966; Schwenk, 1964). The efficiency of inhibitors also depends on the temperature. Yashiro, Oyama, and Tanno (1997) reported for 304 SS the efficiency of inhibitors at 25°C being  $\text{NO}_3^- > \text{MoO}_4^{2-} > \text{H}_2\text{PO}_4^- + \text{HPO}_4^{2-}$  (molar ratio 1/1)  $> \text{SO}_4^{2-}$ . However, at 75°C and 150°C, the efficiency changed as  $\text{H}_2\text{PO}_4^- + \text{HPO}_4^{2-}$  (molar ratio 1/1)  $> \text{MoO}_4^{2-} > \text{SO}_4^{2-} > \text{NO}_3^-$ . Zuo, Wang, Zhao, and Hiong (2002) reported the following inhibitors ranking for 316L SS at 25°C:  $\text{PO}_4^{3-} > \text{CrO}_4^{2-} > \text{SO}_4^{2-} > \text{NO}_3^-$ . It is also observed that efficient inhibitors of the chloride-induced pitting corrosion, such as  $\text{NO}_3^-$  and  $\text{MoO}_4^{2-}$ , are unable to inhibit the localized attack in the presence of bromide ions (Schwenk, 1964; Sugimoto & Sawada, 1976). Organic surface active species are reported to inhibit pitting corrosion of 304 SS. Their efficiency seems to be related to the ability to form a hemimicellar layer on the passive film surface (DeBerry & Vielbeck, 1988). Inhibiting species may also be incorporated on the passive film by proper surface treatments (Breslin, Chen, & Mansfeld, 1997; Burstein & Souto, 2004; Gluszek, Freeman, Baron, & Kubicki, 1985). Pitting corrosion may be photoinhibited by illumination with ultraviolet (UV) light (Fujimoto, Yamada, & Shibata, 1998; MacDonald & Heaney, 2000; MacDonald, Sikora, Balmas, & Alkire, 1996). Summarizing the preceding review, the inhibitor efficiency depends on many factors, such as alloy composition, surface treatment, potential range, aggressive anion identity and concentration, solution pH, temperature, etc.

### 3. Stages of localized corrosion and critical conditions to proceed

Distinction of different stages in localized corrosion is important as inhibitors may act in one or more of these stages. The local chemistry within pits and crevices of stainless alloys is characterized by a low pH and a high chloride concentration (reaching saturation in most cases) (Burstein, Liu, Souto, & Vines, 2004; Frankel, 1998). Localized corrosion proceeds in a series of steps (Burstein et al., 2004). The first



**Figure 1** Typical anodic polarization curve of a SS in a chloride plus nitrate solution showing the presence of  $E_p$  and  $E_i$ . The effect of the ohmic drop within a crevice is schematically shown.

step is pitting nucleation, which is related to passive film breakdown due to the formation of a chloride salt nucleus. This nucleus is able to propagate until it is dispersed into the bulk environment. Sulfide inclusions are reported to be preferential sites for pit nucleation in SS (Sedriks, 1996). The embryonic pit will repassivate unless the dissolving metal chloride lies in a position enabling a restricted mass transport. In this case, the site remains saturated and a diffusion gradient to the exterior bulk solution is established, giving rise to the metastable pit growth. The metastable pit propagates under diffusion control. At potentials above  $E_p$ , the metastable pit is able to reach a critical size to become a stable growing pit. At this stage, the geometry of the pit itself is sufficient to sustain its own diffusion control (Burstein et al., 2004). Metastable pitting is more easily stabilized in an occluded region like a crevice, giving rise to crevice corrosion (Szkłarska-Smialowska, 2005). Stable crevice corrosion occurs at the sites where a row of metastable pits formed at a critical distance from the crevice mouth (Kehler & Scully, 2005).

Another important issue is the definition of the critical conditions to be fulfilled for stable localized corrosion to occur. Inhibitors should act by avoiding the occurrence of these conditions, or at least by increasing the difficulty to reach them. There is a critical value of the product  $x \cdot i$  to be exceeded for the stable propagation of the localized corrosion to occur (where  $x$  is the diffusion path and  $i$  is the current density) (Galvele, 1976). For the chloride-induced pitting corrosion of SS, the reported value of  $x \cdot i$  is 0.3–0.6 A/m (Frankel, 1998). For pitting corrosion,  $x$  is assimilated to the pit radius. The critical conditions are more easily attained in a crevice, where  $x$  is larger.

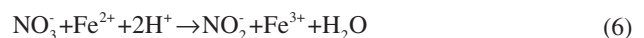
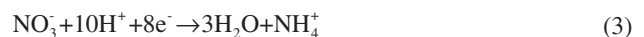
#### 4. Inhibitors for the localized corrosion of stainless alloys

Chloride ion is the main aggressive species causing localized corrosion of stainless alloys (Szkłarska-Smialowska, 2005). Bromide ion is also detrimental. However, it is generally less aggressive than chloride (Abd El Meguid & Abd El Latif, 2004; Rebak, Koon, Cotner, & Crook, 1999). As long as molybdenum contents of the alloys increase, bromide ion becomes more detrimental than chloride (Kaneko & Isaacs, 2002). Fluoride ion promotes uniform rather than localized corrosion, and it may show a slight inhibiting effect in low chloride solutions (Carranza, Rodríguez, & Rebak, 2007; Cragolino & Sridhar, 1991).

The hydroxyl anion is the precursor of the passive film. The dehydration of  $\text{OH}^-$  leads to the passive film build up and its further aging (Marcus & Maurice, 2000). Consequently,  $\text{OH}^-$  is the strongest inhibitor of localized corrosion (Leckie & Uhlig, 1966; Schwenk, 1964; Wang & Newman, 2004).  $E_p$  increases with  $\text{OH}^-$  concentration in the alkaline range of pH. The critical value of  $x \cdot i$  increases with pH, making it more difficult to attain critical chemistry (Galvele, 1976; Keitelman, Gravano, & Galvele, 1984). Pitting corrosion of 300 SS series is completely inhibited for  $\text{OH}^-$  to  $\text{Cl}^-$  concentration ratios of approximately 0.03–0.05. However, crevice

corrosion in alkaline environments cannot be ruled out (Wang & Newman, 2004).

Nitrate ion was one of the former species to be tested as an inhibitor of the chloride-induced pitting corrosion of SS. Increasing additions of  $\text{NO}_3^-$  shift  $E_p$  to higher values, causes the appearance of  $E_p$ , and reduces both the pitting current density and the potential range of pitting corrosion (Leckie & Uhlig, 1966; Rozenfeld & Danilov, 1967; Schwenk, 1964). Keitelman and Galvele (1982) indicate  $E_i$  is the Flade potential of the alloy in the pit solution. The passivation of growing pits above  $E_i$  occurs under a metal chloride film. Newman and Ajjawi (1986) relate this fact to redox reactions, such as the reduction of nitrate within the salt film, coupled with an increase in the pH of the salt environment with increasing potentials. If the salt film behaves as an ohmic conductor, its thickness will increase with potential. Thick ohmic salt films are less acidic than thin ones because of the different balance of electromigration and diffusion of  $\text{H}^+$  within the film (Beck, 1982). Reaching the critical pH for the alloy passivation would be easier in the presence of such a film, water being the passivating agent (Newman & Ajjawi, 1986; Newman & Shahrabi, 1987). The presence of  $E_i$  complicates the determination CPT of SS in  $\text{NO}_3^-$  plus  $\text{Cl}^-$  solutions. Yashiro et al. (1997) indicate that  $\text{NO}_3^-$  is an effective inhibitor in oxidizing conditions (at high anodic potentials) as CPT of 304 SS increases with the applied potential in the presence of nitrate ions. It should be considered that as the  $\text{NO}_3^-$  to  $\text{Cl}^-$  ratio increases,  $E_i$  decreases and  $E_p$  increases, leading to a reduction of the range of pitting corrosion. A distinction should be made between these two effects, as  $\text{NO}_3^-$  is able to act both at low and at high potentials.  $\text{NO}_3^-$  retards nucleation and reduces the propagation rates of metastable pitting of SS (Zuo et al., 2002). The effects at low potentials have been attributed to different mechanisms. Newman and Shahrabi (1987) postulate the surface enrichment of nitrogen atoms at weak sites. In this way, the effect of nitrate ion as an inhibitor would be similar to that of alloyed nitrogen. Nitrate ion may be reduced either to ammonia or to elemental nitrogen, consuming protons and producing water, Eqs. (3) and (4). Reduction of nitrates to nitrogen has been confirmed in other systems (de Wexler & Galvele, 1974). Nitrogen may block preferential dissolution sites on the surface (active kinks), or being further reduced to ammonia, with proton consumption, Eq. (5). Nitrate ion may also form a redox couple with  $\text{Fe}^{2+}$ , consuming protons at low pH, Eq. (6), and assisting in the formation of a hydroxide barrier film at high pH (Newman & Shahrabi, 1987).



Brossia and Kelly (1998) analyzed the crevice solution composition of 304 and 316 SS, ruling out the possibility of

reduction of nitrate to  $\text{NO}_2^-$  or  $\text{NH}_4^+$ , as these species were not detected. Reduction of  $\text{NO}_3^-$  to elemental N could not be ruled out. These authors reported a more aggressive crevice solution in the presence of  $\text{NO}_3^-$ , but they state that this modification of the occluded site solution is not enough to explain the inhibiting effect of  $\text{NO}_3^-$ . The supporting electrolyte effect is also invoked for explaining inhibition by  $\text{NO}_3^-$  (Zuo et al., 2002). Ilevbare et al. (2005) support the view of a competitive effect between  $\text{NO}_3^-$  and  $\text{Cl}^-$ , determining unlikely an inhibition mechanism solely based on the adsorption of  $\text{NO}_3^-$  or elemental N on weak sites. A mechanism based on the pH increase by any reduction reaction of  $\text{NO}_3^-$  would be consistent with their results on crevice corrosion of alloy 22. Recently, Lillard, Vasquez, and Bahr (2011) studied the influence of nitrate ions on the repassivation kinetics of 304L SS by scratching tests. In the presence of nitrate ions the film formation occurs more rapidly as compared to chloride. The presence of nitrate ions also led to thinner films (<0.6 nm) and higher electric field strengths at early times. Increasing the chloride concentration from 0.1 to 0.9 M result in thicker passive films (0.6–2.2 nm) and lower electric field strengths.

Sulfate ion has also been extensively studied as a localized corrosion inhibitor. It may enhance localized corrosion when present in small amounts in chloride solutions (Cragolino & Sridhar, 1991). Sulfate cannot be reduced within a low pH environment. Supporting electrolyte effect, including competitive adsorption of chloride and sulfate on the SS surface is usually postulated (Abd El Meguid & Abd El Latif, 2004; Brossia & Kelly, 1998; Ürgen & Çakir, 1991; Yashiro et al., 1997). Thus, the critical chloride concentration needed for the film breakdown is more difficult to reach. The inhibition efficiency of sulfate ion decreases with temperature, which is interpreted as a decrease of its adsorption rate (Ürgen & Çakir, 1991). However,  $\text{HSO}_4^-$  adsorbs more strongly than  $\text{SO}_4^{2-}$  on SS, and no inhibition is observed in acidic solutions at which  $\text{HSO}_4^-$  predominates. An alternative explanation is the pH buffering effect of  $\text{SO}_4^{2-}$  (Yashiro et al., 1997). The presence of sulfate causes the distribution of available pit sites to be shifted to higher potentials. Pit nucleation and metastable and stable pit propagation are inhibited. Sulfate ions also reduce the solubility of the metal cations produced by dissolution in the pit solution (Pistorius & Burstein, 1992). Newman and Ajjawi (1986) suggest that passivation may occur below precipitated sulfate films by inward diffusion of water. Sulfate ion is able to accumulate preferentially at the metal/solution interface by migration due to its higher charge with respect to chloride ion. It may cause the deactivation of growing pits. Diffusion of sulfate ions out of the pit may cause an oscillating process of activation deactivation (Galvele, 1976).

Chromate, molybdate, and tungstate anions have been studied as corrosion inhibitors and their behaviors are frequently compared to those of Cr, Mo, and W as alloying elements. These anions may inhibit pitting corrosion by changing the anion selective character of the passive film to cation selective, preventing the ingress of chloride ions (Sakashita & Sato, 1978). The reported inhibitor efficiency is  $\text{CrO}_4^{2-} > \text{MoO}_4^{2-} > \text{WO}_4^{2-}$  (Gluszek et al., 1985; Ilevbare & Burstein, 2003; Rabaçal Alentejano & Vieira Aoki, 2004). When passive films

of ferritic SS are exposed to chromate, molybdate, or tungstate solutions their properties are significantly affected. The film thickness and their oxygen contents increase with the oxidizing power of the species as  $\text{CrO}_4^{2-} > \text{MoO}_4^{2-} > \text{WO}_4^{2-}$  (Gluszek et al., 1985). It has been proposed that chromate, molybdate, and tungstate ions are reduced forming dense precipitates that function by an ohmic blocking action (Ilevbare & Burstein, 2003; Newman & Ajjawi, 1986). Reduction products might be preferentially deposited at the sites of inclusions, as these sites are supposed to be more reactive than the rest of the metal surface. Chromate and molybdate ions affect both the nucleation of pitting and metastable pitting of 304 and 316 SS, by reducing the numbers and sizes of these events (Ilevbare & Burstein, 2003).  $\text{CrO}_4^{2-}$  and  $\text{MoO}_4^{2-}$  may reduce the local acidity at the sites where they react according to Eqs. (7) and (8), respectively. This would affect the transition from nucleation to metastable pitting, as a low pH is important to maintain the aggressiveness necessary for pit development (Ilevbare & Burstein, 2003; Yashiro et al., 1997). The  $\text{CrO}_4^{2-}/\text{Cr}_2\text{O}_7^{2-}$  equilibrium should be taken into account, as  $\text{CrO}_4^{2-}$  may reduce solution acidity (Zuo et al., 2002). The deposition of the reduction products ( $\text{Cr}_2\text{O}_3$  and  $\text{MoO}_2$ ) is also proposed as an inhibiting mechanism.  $\text{Cr}^{3+}$  and  $\text{Mo}^{4+}$  may be built into the film (Devasenapathi & Raja, 1996; Gluszek et al., 1985; Sugimoto & Sawada, 1976; Zuo et al., 2002).



Chromate ion is a stronger oxidizer than molybdate. The reduction rate of molybdate ion depends on pH and temperature. It becomes significant below pH 4 and increases with the decrease of pH and the increase of temperature (Ürgen & Çakir, 1991). Molybdates may polymerize when the pH is lowered below ca 6. Condensed species are formed consuming protons, Eqs. (9) and (10) (Ürgen & Çakir, 1991; Yashiro et al., 1997). Other polymeric species of molybdate are reported elsewhere, being longer chains for decreasing pH values (Pourbaix, 1974). Molybdic acid ( $\text{HMoO}_4^-$ ) may form and precipitate in a propagating pit, resulting in the pit repassivation due to blocking of active sites (Ürgen & Çakir, 1991).



Potentiostatic testing of pure Mo produces  $\text{MoO}_4^{2-}$  when tested under conditions corresponding to those initially found in a localized corrosion process (Lillard, Jurinski, & Scully, 1994). It has been suggested that addition of molybdate ions to the solution may have an inhibiting effect on the localized corrosion similar to that of molybdenum in the alloy (Newman, 1985; Sugimoto & Sawada, 1976; Ürgen & Çakir, 1991). However, other researchers indicate that  $\text{MoO}_4^{2-}$  released in an active crevice does not fully account for the inhibiting effects of alloyed molybdenum (Lillard et al., 1994). Molybdenum

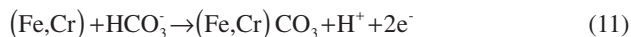


is detected as  $\text{Mo}^{6+}$  in passive films of SS, and it is thought to be stable as  $\text{MoO}_4^{2-}$  (Sugimoto & Sawada, 1976). In passive films of Ni-Cr-Mo alloys, Mo is detected in a range of oxidation states ( $\text{Mo}^0$ ,  $\text{Mo}^{4+}$ ,  $\text{Mo}^{5+}$ , and  $\text{Mo}^{6+}$ ) (Lloyd, Noël, McIntyre, & Shoosmith, 2004). XPS depth profiles of 304 SS after polarization in chloride plus molybdate solutions showed that Mo was incorporated in the passive film. It is detected throughout the film as  $\text{Mo}^{4+}$ ,  $\text{Mo}^{5+}$ , and  $\text{Mo}^{6+}$  (Yashiro et al., 1997). It has also been found as  $\text{Mo}^{3+}$  and  $\text{Mo}^{4+}$  in the inner layers (Devasenapathi & Raja, 1996).  $\text{MoO}_4^{2-}$  suppresses both pit initiation and growth in 20Cr-25Ni-xMo SS in NaCl solutions (Sugimoto & Sawada, 1976). Molybdate ion is effective in reducing pit growth of active pits below a critical size. This suggests that molybdate ion may act in an early stage of pit growth, before a local chemistry is well established within the pit (Lillard et al., 1994; Rujini & Ives, 1989). Addition of  $\text{MoO}_4^{2-}$  to ocean water delayed crevice corrosion initiation of alloy 625 and reduced the propagation rates (Lillard et al., 1994). Wanklyn states that crevice corrosion inhibition on SS is due to the precipitation of  $\text{Mo}^{4+}$  oxide films by reduction of  $\text{Mo}^{6+}$ , Eq. (8) (Wanklyn, 1981).  $\text{MoO}_4^{2-}$  is an effective pitting corrosion inhibitor of 304 SS in the presence of chlorides, in the broad temperature range from 25°C to 150°C (Ürgen & Çakir, 1991; Yashiro et al., 1997). The effectiveness of molybdate ions increases with temperature. The precipitation of molybdic acid and the reduction of molybdate ions are accelerated at increasing temperatures and decreasing pH. It can be claimed that one or both of these reactions, Eqs. (8) and (10), is responsible for the increasing effectiveness of molybdate ions with temperature (Ürgen & Çakir, 1991). In addition to the reduction of local acidity, it is thought that  $\text{MoO}_4^{2-}$  preferentially adsorbs on the SS surface precluding the adsorption of  $\text{Cl}^-$  at the initial stages of pitting. Adsorption of  $\text{MoO}_4^{2-}$  is considered to proceed according to a Freundlich type of isotherm (Sugimoto & Sawada, 1976). If blocking the active sites by adsorption is the main inhibition mechanism, the increase of temperature would generally lead to a decrease of the adsorption rate, and therefore a decrease of the inhibiting effect. However, the contrary is observed indicating that adsorption does not fully explain the inhibiting effect of molybdate anion (Ürgen & Çakir, 1991).

Anions of weak inorganic acids, such as phosphates, carbonates, borates, silicates, etc., are known for being beneficial on pitting corrosion. This is due to their pH buffering effect, avoiding or making more difficult the development of a critical chemistry (Galvele, 1976).

Yashiro et al. (1997) showed that the mixture  $\text{H}_2\text{PO}_4^- + \text{HPO}_4^{2-}$  in a molar ratio 1/1 is an effective inhibitor of pitting corrosion of 304 SS in chloride solutions. Its effectiveness increases with temperature. Phosphorous is incorporated in the outer part of the passive film. Zuo et al. (2002) reported that  $\text{PO}_4^{3-}$  is the best among tested inhibitors for retarding nucleation and reducing the propagation rates of metastable pitting of 316L SS. Hydrolysis of  $\text{PO}_4^{3-}$ ,  $\text{HPO}_4^{2-}$ , and  $\text{H}_2\text{PO}_4^-$  is expected in the pit solution, preventing the acidification and promoting passivation. Phosphates may also act by forming insoluble salts with  $\text{Cr}^{3+}$  and  $\text{Fe}^{3+}$  preventing cation hydrolysis (Yashiro et al., 1997).

The addition of 0.5 M  $\text{HCO}_3^-$  to a 4% NaCl solution completely inhibits the crevice corrosion of 254 SMO SS at 70°C (Abd El Meguid & Abd El Latif, 2004).  $E_p$  of 316L SS increases with increasing the concentration of  $\text{HCO}_3^-$  in a 0.5 M NaCl solution (Park, Pyun, Lee, & Kim, 1999). The formation of a  $(\text{Fe,Cr})\text{CO}_3$  film caused by preferential adsorption of  $\text{HCO}_3^-$  is thought to lead to instantaneous repair of weak sites for pit nucleation (Park et al., 1999). However, Eq. (11) shows that this reaction promotes the local acidification of the pit.



$E_{RP}$  of 316 Ti SS and duplex S318.03 SS slightly increases as the concentrations of borate and silicate ions are increased in pH 9 chloride solutions (Bellanger, 2006). Borate ion is a more effective inhibitor than silicate. Borate or silicate ions buffer the surface at pH 9 avoiding acid pH and dissolution within the pit. These inhibitors may suppress the activity at weak points in the oxide. A blocking effect by competitive adsorption with chloride ions is also suggested (Bellanger, 2006).

Small additions of surface active species increases  $E_p$  of 304 SS in chloride solutions (DeBerry & Vielbeck, 1986, 1988; Vielbeck & DeBerry, 1984). Inhibitors based on the *N*-acylamino acid, such as *N*-lauroylsarcosine (NLS) are strongly adsorbed on the passive film surface over a wide potential range. NLS may act as a surface buffering agent avoiding or delaying the critical conditions for pit initiation (DeBerry & Vielbeck, 1986). A hemimicellar layer may form on the passive film surface acting as a barrier towards the ingress of aggressive anions (DeBerry & Vielbeck, 1988). However, once the passive film has broken down the inhibitor is not effective anymore.  $E_{RP}$  is not affected by the presence of NLS (Vielbeck & DeBerry, 1984).

Inhibiting species such as chromate, molybdate, tungstate, cerium, and silicate ions, may also be incorporated in the passive film by surface treatments leading to a more corrosion resistant material (Breslin et al., 1997; Burstein & Souto, 2004; Gluszek et al., 1985). These techniques have been proven useful in several SS of the 300 series.

The local breakdown of passive films may be inhibited by illumination with UV light (Fujimoto et al., 1998; MacDonald & Heaney, 2000; MacDonald et al., 1996). This phenomenon, called photoinhibition, occurs due to the semiconducting character of the films formed on stainless alloys.  $E_p$  increases under illumination, and the number of pits and the rate of metastable events decrease. However,  $E_{RP}$  is not affected by UV illumination.

## 5. Mechanisms of inhibition of the localized corrosion

The idea of a relationship between the oxidizing power of the anions and their inhibiting efficiency has been discarded (Rozenfeld & Danilov, 1967). The first explanation given to the inhibition phenomena was related to the competitive adsorption of inhibitors and chloride anions on the metal surface

(Leckie & Uhlig, 1966; Matsuda & Uhlig, 1964; Rozenfeld & Danilov, 1967; Schwenk, 1964). However, these species should reach the alloy surface by migration before they may adsorb. Anions migrate towards the alloy surface under the influence of an electric field created by the excess of metallic cations inside the pit. For anions of different charge, those with the highest one will be preferentially accumulated at the alloy/solution interface (Galvele, 1976). Thus, it may be predicted that, for instance,  $\text{CO}_3^{2-}$  and  $\text{PO}_4^{3-}$  will be more effective inhibitors than  $\text{HCO}_3^-$  and  $\text{HPO}_4^{2-}$ . It is important to note that although the anions accumulate at the alloy surface by migration, there is a concentration gradient pulling them out of the pit. The supporting electrolyte effect consists of the competitive migration and adsorption of inhibitor and chloride species on the metal surface, preventing the increase of chloride concentration to a critical value. Sometimes, it is also referred to as a diluting effect. Any of the considered inhibitors may act in this way. The ionic conductivities and diffusion coefficients of the species are important to assess their ability to reach the alloy surface and being pulled out by diffusion (Ilevbare et al., 2005; Zuo et al., 2002). The hydroxyl anion is the only one showing a diffusion coefficient significantly larger than those of other species. Table 2 shows the diffusion coefficients of selected species. According to Szklarska-Smialowska (2005), the competitive adsorption of anions on a metal surface is well represented by a Temkin's isotherm. The metal surface is inhomogeneous and the lateral repulsive interactions increase with coverage. The Temkin's assumption of a heat of adsorption decreasing with coverage is appropriate in this case.

The inhibitive effect may be affected by the size and the bond strength of the adsorbed molecule and in dislodging

**Table 2** Diffusion coefficients at infinite dilution of selected anions at 25°C (Lide, 2004).

Anion	Diffusion coefficient $10^{-5}$ ( $\text{cm}^2 \text{s}^{-1}$ )
$\text{Cl}^-$	2.032
$\text{Br}^-$	2.080
$\text{F}^-$	1.475
$\text{HF}_2^-$	1.997
$\text{OH}^-$	5.273
$\text{NO}_3^-$	1.902
$\text{SO}_4^{2-}$	1.065
$\text{HSO}_4^-$	1.385
$\text{ClO}_3^-$	1.720
$\text{ClO}_4^-$	1.792
$\text{CrO}_4^{2-}$	1.132
$\text{MoO}_4^{2-}$	1.984
$\text{WO}_4^{2-}$	0.919
$\text{CO}_3^{2-}$	0.923
$\text{HCO}_3^-$	1.185
$\text{PO}_4^{3-}$	0.824
$\text{HPO}_4^{2-}$	0.759
$\text{H}_2\text{PO}_4^-$	0.959
Acetate	1.089
Citrate	0.623
Formate	1.454
Oxalate	0.987

chloride from the sites through which it preferentially penetrates the passive oxide layer (Bellanger, 2006; Ilevbare & Burstein, 2003; Ilevbare et al., 2005). An inhibitor may penetrate or be pulled through the oxide film under the influence of the electric field provided that it is not much larger than  $\text{Cl}^-$ . Once the inhibitor migrates through the oxide film, either of two things could occur: the species may react with the inclusions to form a thin layer of insoluble compounds/complexes on the surface of the inclusion, preventing the formation of the metal chloride, and the further reaction of the inhibitor and the inclusions so that film rupture does not occur anymore; or the inhibitor, due to its larger volume compared with  $\text{Cl}^-$ , reduces the amount of  $\text{Cl}^-$  ions (Ilevbare & Burstein, 2003). Table 3 shows the ionic radius of selected species. The considered anions have an ionic radius similar to that of chloride.

The pH buffering capacity of anions of weak acid salts is based on the dissociation constant of the corresponding acid. Those with large  $\text{p}K_a$  values will be more effective in avoiding the development of a locally aggressive chemistry. Table 4 shows the dissociation constants of selected acids. The critical value of  $x_i$  increases with the addition of weak acid anions, causing the increase of  $E_p$ . The localized corrosion is completely inhibited for sufficiently large inhibitor to chloride concentration ratios (Galvele, 1976).

Oxyanions such as chromate, molybdate, and tungstate may inhibit pitting corrosion by changing the anion selective

**Table 3** Ionic radius of selected anions (Heslop & Jones, 1976).

Anion	Ionic radius (pm)
$\text{Cl}^-$	181
$\text{SO}_4^{2-}$	230
$\text{NO}_3^-$	189
$\text{CO}_3^{2-}$	185
$\text{OH}^-$	182
$\text{CrO}_4^{2-}$	242
$\text{MoO}_4^{2-}$	254
$\text{WO}_4^{2-}$	258
$\text{PO}_4^{3-}$	238

**Table 4** Dissociation constants of selected acids at 25°C (Lide, 2004).

Acid	$\text{p}K_{a1}/\text{p}K_{a2}/\text{p}K_{a3}/\text{p}K_{a4}$
HCl	-8
$\text{H}_2\text{SO}_4$	-3/1.99
$\text{HNO}_3$	-2
$\text{HClO}_4$	-1.6 (20°C)
$\text{H}_3\text{PO}_4$	2.16/7.21/12.32
HF	3.20
$\text{H}_2\text{CO}_3$	6.35/10.33
$\text{H}_3\text{BO}_3$	9.27/>14 (20°C)
$\text{H}_2\text{CrO}_4$	0.74/6.49
$\text{H}_4\text{SiO}_4$	9.9/11.8/12/12 (30°C)
Oxalic	1.25/3.81
Formic	3.75
Acetic	4.736

character of the film to cation selective, preventing the ingress of chloride ions (Sakashita & Sato, 1978). Surface active species are thought to act by forming a hemimicellar layer on the passive film surface, being a physical and electrostatic barrier towards the ingress of aggressive anions. They may also act by local pH buffering (DeBerry & Vielbeck, 1988). Inhibiting species incorporated to the passive film by surface treatments may form thicker and more protective films (Gluszek et al., 1985), may reduce the oxygen reduction kinetic on the film (Breslin et al., 1997), or may act by a specific action in the pit nucleation sites (Burstein & Souto, 2004). Photoinhibition of pitting corrosion by UV illumination is attributed to the modification of the passive film, the electric field in the film, and changes in the electronic structure on the film/solution interface (Fujimoto et al., 1998; MacDonald & Heaney, 2000; MacDonald et al., 1996).

## 6. Cathodic reactions, limitations, and non-desired effects of inhibitors

Powerful oxidizing inhibitors, such as  $\text{NO}_3^-$ ,  $\text{ClO}_4^-$ , and  $\text{CrO}_4^{2-}$ , may raise the corrosion potential ( $E_{CORR}$ ) up to exceeding  $E_{CRIT}$  leading to localized corrosion. A milder oxidizing species, such as  $\text{MoO}_4^{2-}$ , has shown a detrimental effect on the repassivation of 304 SS in 1 M HCl when present in low concentrations (Devasenapathi & Raja, 1996). This was attributed to an increase in the cathodic reaction rate and a consequent increase in anodic dissolution. Care is to be taken to ensure that the inhibiting effect on the anodic localized kinetics is more beneficial than the undesired strength given to the cathodic kinetics. Most of the reviewed research is related to the inhibition of the local anodic reaction. Acting over the cathodic kinetics is another way of preventing the localized corrosion. Localized corrosion may occur only if  $E_{CORR}$  is above  $E_{CRIT}$ . Eliminating or reducing the concentration of oxidizing species in solution will cause a decrease of  $E_{CORR}$ . This is an obvious but effective way of reducing the likelihood of localized corrosion. Borate and silicate ions exhibit a cathodic inhibition effect, shifting the  $E_{CORR}$  of SS to lower potentials (Bellanger, 2006). Alkaline solutions also reduce the oxygen reduction kinetics (Wang & Newman, 2004).

In the particular case of  $\text{ClO}_3^-$  and  $\text{ClO}_4^-$ , it should be considered that its reduction may lead to the undesired Cl<sup>-</sup> release into the solution (Pourbaix, 1974). The addition of  $\text{HCO}_3^-$  to NaCl solutions causes the pit growth of 316L SS to be retarded in the lateral direction but promoted in the downward direction. In the presence of  $\text{HCO}_3^-$ , the protective (Fe,Cr) $\text{CO}_3$  film is preferentially formed along the pit mouth and walls, rather than at the pit bottom (Park et al., 1999). Addition of  $\text{HCO}_3^-$  in low concentrations may lead to a quicker perforation of walls in practical applications.

The number of candidate inhibitors for certain applications may be very limited based on characteristics other than their inhibiting efficiency. For instance, environmental regulations must be addressed, precluding the use of chromate ions. Inhibitors for service in low level tritiated water are chosen based on their inertness to the radiolysis (Bellanger, 2006).

Inhibitors for reinforced concrete should not affect the curing rate of cement.

## 7. Inhibitors for the chloride-induced crevice corrosion of alloy 22

In the past decade, considerable efforts have been devoted to study the localized corrosion of alloy 22 (UNS N06022) regarding its use as a corrosion resistant barrier of nuclear waste containers (Gordon, 2002). Alloy 22 does not suffer pitting corrosion unless very hot and concentrated chloride solutions are considered (Rodríguez, Stuart, & Rebak, 2007a; Rodríguez, Carranza, Stuart, & Rebak, 2007b). This is because the maximum attainable corrosion current density in the localized solution is limited to a low value ( $<20 \text{ mA/cm}^2$ ). The critical value of  $x \cdot i$  may be only exceeded for long enough crevices (Rodríguez, Carranza, & Rebak, 2010a). Inhibitors and chloride ions are present in the groundwater potentially in contact with the containers. Assessing the effect of different species in solution on the repassivation potential of alloy 22 is of main importance. The effects of anions typically found in groundwater, such as nitrate, sulfate, fluoride, carbonate, bicarbonate ions, and other less common species have been extensively studied, covering different metallurgical conditions of the alloy, temperatures, pH values, etc. The inhibitor to chloride concentration ratio ( $R$ ) is a parameter commonly used in the reviewed studies. In certain cases, there is a critical value ( $R_{CRIT}$ ) above which no crevice corrosion is observed.  $R_{CRIT}$  is related to the effectiveness of a particular inhibitor.

The following empirical observations are reported for stainless alloys in the presence of inhibitors of crevice corrosion (Anderko, Sridhar, & Dunn, 2004):

- In chloride solutions containing a weak inhibitor,  $E_{RC}$  increases slowly as  $R$  increases up to the point where the inhibitor predominates in the solution.
- In chloride solutions containing a strong inhibitor,  $E_{RC}$  rises to high values at relatively low concentrations of the inhibitor.
- In ternary solutions, where a weak inhibitor is added to a binary mixture of chloride plus a strong inhibitor, the concentration of the strong inhibitor required to raise  $E_{RC}$  to high values is less than in the binary mixture.

Dunn & Brossia (2002) and Dunn, Pan, Yang, & Cragolino (2006) investigated the inhibiting effect of nitrate on the crevice corrosion of as welded (ASW) alloy 22 at 95°C. The authors stated that  $R_{CRIT}=0.5$  for ASW alloy 22 in a 0.5 M Cl<sup>-</sup> solution. When crevice corrosion is initiated in a 0.5 M Cl<sup>-</sup> solution, the addition of 0.05 M  $\text{NO}_3^-$  produces a 0.25 V increase of  $E_{RC}$ . These results show that nitrate ion is not only able to inhibit the localized corrosion initiation but also promotes the repassivation of the already developed localized corrosion. Evans et al. (2003) reported a significant increase of  $E_{RC}$  of alloy 22 in 0.5 M  $\text{Ca}(\text{NO}_3)_2$ +5 M  $\text{CaCl}_2$  solution at temperatures from 45°C to 120°C, when compared with  $E_{RC}$  in pure 5 M  $\text{CaCl}_2$  solution. These authors tested mill

annealed (MA) material. Dunn, Yang, Wu, and Cragolino (2004) and Dunn et al. (2005a) studied the effect of nitrate on MA and thermally aged (5 min at 870°C) alloy 22 in 4 M MgCl<sub>2</sub> at 80°C and 110°C. The thermal aging performed may lead to the precipitation of second phases at the grain boundaries and it is thought to simulate a welding process.  $R_{CRIT}$ =0.1 and 0.15 is reported for the MA material at 80°C and 110°C, respectively. For the thermally aged specimens,  $R_{CRIT}$ =0.1 and 0.3 is reported at 80°C and 110°C, respectively.  $R_{CRIT}$ =0.12 is reported for MA alloy 22 in 4 M NaCl at 95°C (Dunn, Pan, Yang, & Cragolino, 2005b).  $R_{CRIT}$  for nitrate ion is not strongly dependent on temperature or chloride concentration, but slightly increases for the aged material at high temperature (Dunn et al., 2004, 2005a). Mishra and Frankel (2008) investigated the effects of nitrate and sulfate ions both individually and in combination.  $R$  rather than the nitrate concentration was found to be the determining factor for the complete inhibition of crevice corrosion.  $R_{CRIT}$ =0.2 was found for nitrate ions at 90°C.  $E_{CR}$  increases linearly with  $\log(\text{NO}_3^-)$  for concentrations below  $R_{CRIT}$  according to Eq. (2). The authors also investigated the effect of nitrate and sulfate ions added together.  $R_{CRIT}$ =0.15 is observed for nitrate ion in 1 M NaCl at 90°C when sulfate ion is present at  $R$ =0.2 and 0.5. This value is slightly lower than  $R_{CRIT}$ =0.2, in the absence of sulfate ions. Kehler, Ilevbare, and Scully (2001) studied the crevice corrosion susceptibility of MA alloys 625 and 22 in 5 M LiCl solutions plus a mixture of nitrates and sulfate ions, at temperatures from 60°C to 95°C. The alloys were tested in 5 M LiCl+0.24 M NaNO<sub>3</sub>+0.26 M NaSO<sub>4</sub> ( $R$ =0.1) and 5 M LiCl+0.024 M NaNO<sub>3</sub>+0.026 M NaSO<sub>4</sub> ( $R$ =0.01) solutions.  $E_{RC}$  increases significantly for  $R$ =0.01 and  $R$ =0.1 as the temperature is decreased for both alloys.  $E_C$  and  $E_{RC}$  are stronger functions of  $R$  and temperature for alloy 22 than for alloy 625.

Yilmaz, Pasupathi, and Rebak (2005) performed constant potential tests above  $E_{RC}$  for ASW alloy 22 in chloride plus nitrate brines at 100°C. They observed three characteristic domains: (1) nucleation, (2) growth, and (3) stifling and arrest of crevice corrosion. Smaller crevice corrosion sites are developed in electrolytes solutions with a higher  $R$  than in those with a lower  $R$ . The increase of  $R$  also leads to a shorter stage of propagation (2) and lower crevice corrosion current density.

The inhibiting effect of nitrate ions on the localized corrosion of alloy 22 is also verified in hot concentrated brines. Rodríguez et al. (2007b) reported that creviced specimens of alloy 22 were free from localized corrosion after 720 days of immersion in 5 M CaCl<sub>2</sub>+5 M Ca(NO<sub>3</sub>)<sub>2</sub> brines at 100°C and 120°C. Creviced alloy 22 is also reported to be free from localized corrosion after 20 months of immersion in 18 M CaCl<sub>2</sub>+9 M Ca(NO<sub>3</sub>)<sub>2</sub> brine ( $R$ =0.5) at 155°C. However, pitting corrosion is observed after immersion in 18 M CaCl<sub>2</sub>+0.9 M Ca(NO<sub>3</sub>)<sub>2</sub> ( $R$ =0.05) brine at 155°C (Rodríguez et al., 2007a). Crevice corrosion does not occur in such concentrated brines, but only pitting. However  $R$  is still a relevant parameter in these conditions.

Ilevbare (2006) studied the effect of sulfate ion on the crevice corrosion of MA alloy 22 in 4 M NaCl at temperatures

from 45°C to 105°C. Na<sub>2</sub>SO<sub>4</sub> was added to reach  $R$ =0.01 and 0.1. No crevice corrosion was observed at 45°C. At 60°C,  $E_{RC}$  increases more than 0.6 V for  $R$ =0.1, and more than 0.3 V for  $R$ =0.01. At temperatures of 75°C and higher no  $E_{RC}$  increase is detected and the effect of sulfate ion is only observable by the less severe localized attack. A complete inhibition of crevice corrosion is not reported for the tested  $R$  values (Ilevbare, 2006). Mishra and Frankel (2008) reported  $R_{CRIT}$ =1.5 and 0.8 for 1 M and 0.1 M NaCl, respectively, at 90°C. Dunn et al. (2004, 2005a) reported an  $E_{RC}$  increase at  $R$ =0.5 for thermally aged (5 min at 870°C) alloy 22 in 0.5 M NaCl, at 95°C. However, a complete inhibition by sulfate ions is not reported.

The inhibiting effects of carbonate and bicarbonate ions were evaluated in 0.5 M NaCl at 95°C, using thermally aged (5 min at 870°C) alloy 22 specimens (Dunn et al., 2004, 2005a). Inhibition of crevice corrosion was observed at  $R_{CRIT}$ =0.05 for carbonate ion, and at  $R_{CRIT}$ =0.2 for bicarbonate ion. Dunn et al. (2004, 2005a) suggested that CO<sub>3</sub><sup>2-</sup> is as effective as NO<sub>3</sub><sup>-</sup> for inhibiting localized corrosion.

Carranza et al. (2007) indicate that although fluoride ion is detrimental for the passive dissolution of alloy 22, it is able to mitigate and inhibit crevice corrosion for sufficiently high  $R$  values.  $R_{CRIT}$  from 5 to 10 are reported for alloy 22 in 0.001 M, 0.01 M, and 0.1 M NaCl solutions of pH 6, at 90°C.

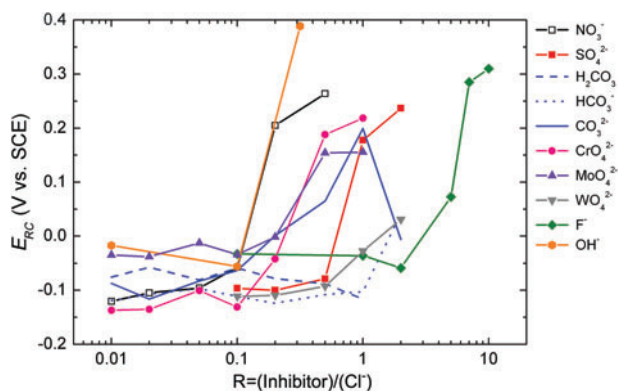
Carranza, Rincón Ortíz, Rodríguez, and Rebak (2009) studied the effect of silicate ions on the crevice corrosion of alloy 22 in 0.01 M, 0.1 M, and 1 M NaCl solutions at 90°C. Crevice corrosion of alloy 22 was inhibited in all the testing solutions with pH≥12.5, regardless of the presence of silicate ions. This effect was attributed only to the high solution pH obtained by the silicate ion hydrolysis. Inhibition was independent of  $R$ , but only dependent on the concentration of the hydroxyl ion.

Miyagusuku, Carranza, and Rebak (2010, 2011) studied the effect of phosphate ion on the crevice corrosion of alloy 22 in near neutral 1 M NaCl solutions at 90°C. They determined  $R_{CRIT}$ =0.3 by two different testing methods. These results indicate that phosphate ions have an inhibiting efficiency similar to that of nitrate ions.

Organic acids are reported to be weak inhibitors of the crevice corrosion of alloy 22 (Carranza, Giordano, Rodríguez, & Rebak, 2008).  $R_{CRIT}$ =2 is reported for citric and oxalic acids, whereas  $R_{CRIT}$ =10 is reported for acetic acid in 0.01 M, 0.1 M, and 1 M chloride solutions at 90°C.

Rincón Ortíz, Rodríguez, Carranza, and Rebak (2011) analyzed the efficiency of a wide variety of inhibitors of the crevice corrosion of alloy 22 in 0.1 M and 1 M NaCl at 90°C. The considered species were classified in three different groups according to their  $R_{CRIT}$  value: (a) effective inhibitors, such as hydroxyl, nitrate, and phosphate ions ( $R_{CRIT}$ ≤0.3); (b) moderately effective inhibitors, such as sulfate, carbonate, chromate, and molybdate ( $2 > R_{CRIT} > 0.3$ ); and (c) weak inhibitors, such as fluoride, organic acids, and possibly bicarbonate and carbonic acid ( $R_{CRIT}$ ≥2). Figures 2 and 3 show  $E_{RC}$  for alloy 22 as a function of  $R$  for different inhibitors in 0.1 M and 1 M chloride solutions, respectively, at 90°C.  $R_{CRIT}$  is determined at the sudden increase of  $E_{RC}$  and according to the visual and microscope observation of the tested specimens.  $E_{RC}$  remains



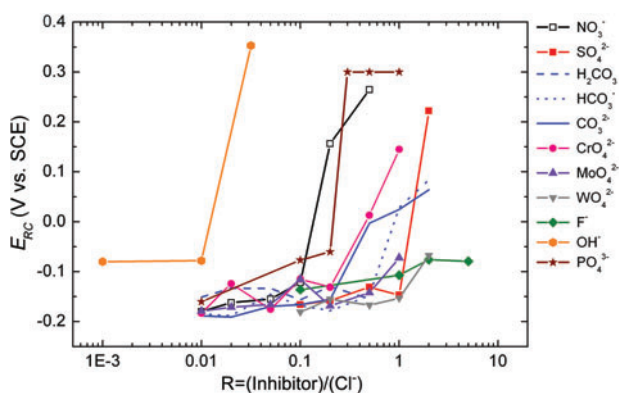


**Figure 2**  $E_{RC}$  as a function of  $R$  for alloy 22 in 0.1 M chloride solutions with different contents of inhibitors, at 90°C (Rincón Ortíz, 2011).

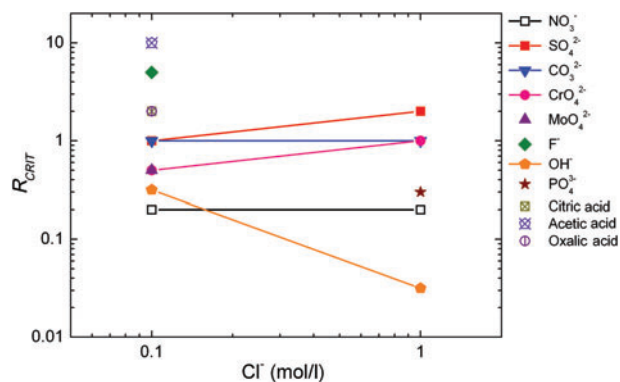
constant or slightly increases below  $R_{CRIT}$ . Carbonate ion is the only species from the equilibrium  $\text{CO}_3^{2-}/\text{HCO}_3^-/\text{H}_2\text{CO}_3$  able to completely inhibit the crevice corrosion of alloy 22 in 0.1 M and 1 M NaCl, at 90°C. The presence of an anodic peak above the passive range may lead to an unreal decrease of  $E_{RC}$  as  $R$  increases, as observed for the carbonate ion (Figure 2). The reported inhibitor efficiency of oxyanions for pitting corrosion of stainless steels,  $\text{CrO}_4^{2-} > \text{MoO}_4^{2-} > \text{WO}_4^{2-}$  (Gluszek et al. 1985; Ilevbare & Burstein, 2003; Rabaçal Alentejano & Vieira Aoki, 2004) is also observed for the crevice corrosion of alloy 22 (Rincón Ortíz, 2011).

Figure 4 shows  $R_{CRIT}$  as a function of the chloride concentration of the solution for different inhibitors.  $R_{CRIT}$  remains constant or slightly increases as the chloride concentration increases for all the tested inhibitors with the only exception of the hydroxyl ion. In this case, the complete inhibition was only dependent on the concentration of the hydroxyl ion, regardless of the chloride concentration (Carranza et al., 2009).

The parameter  $R$  has been shown to be effective in most of the cases for characterizing the effect of crevice corrosion



**Figure 3**  $E_{RC}$  as a function of  $R$  for alloy 22 in 1 M chloride solutions with different contents of inhibitors, at 90°C (Rincón Ortíz, 2011).



**Figure 4**  $R_{CRIT}$  for different inhibitors as a function of the chloride concentration of the solutions for alloy 22, at 90°C (Rincón Ortíz, 2011).

inhibitors of alloy 22. However,  $R$  cannot be used to predict the localized corrosion inhibition in environmental waters, as bacteria and fungi can reduce or assimilate corrosion inhibiting anions such as nitrate and sulfate, altering anion chemistry and concentration (Little, 2003).

The same inhibition mechanisms reviewed regarding the localized corrosion of stainless alloys may be applicable to the crevice corrosion of alloy 22. However, some differences may arise as the critical crevice solution for alloy 22 is much more aggressive than for stainless steels (Rodríguez, Carranza, & Rebak, 2010b). Rebak (2006) propose four ways in which a crevice corrosion inhibitor of alloy 22 may act:

- Stabilization of the  $\text{Cr}_2\text{O}_3$ -rich passive film by maintaining an oxidizing environment inside the crevice.
- Reduction of the inhibitor to a lower oxidation state along with protons consumption.
- Reduction of the general corrosion rate in the creviced area.
- Sequestration of protons released by the hydrochloric acid due to a lower dissociation constant of the corresponding acid.

The effective inhibitors act in many of these proposed ways at the same time. The moderately effective inhibitors may act in two of these ways, whereas the weak inhibitors are expected to act only by sequestering protons from the HCl solution in the crevice (Rincón Ortíz et al., 2011). These four ways of inhibition are not independent from each other. For instance, an inhibitor consuming or sequestering protons will also lead to a reduction of the general corrosion rate of the alloy; an inhibitor which reduces to a lower oxidation state will also generate an oxidizing environment. The reduction of the general corrosion rate may be related to the supporting electrolyte effect, whereas the sequestration of protons is related to the pH buffering effect.

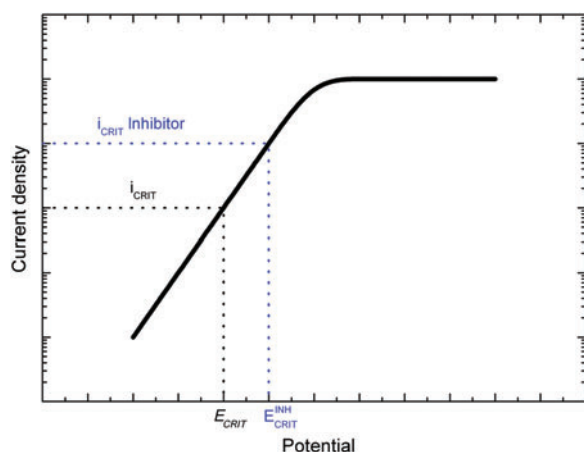
It should be noted that hydroxyl, nitrate, and phosphate ions are the most powerful inhibitors of the crevice corrosion of alloy 22. However, the mechanisms by which they act cannot be the same. Hydroxyl ion is the precursor of passive

film and its depletion leads to the stabilization of the localized corrosion. It cannot be reduced to a lower oxidation state, but it has a direct neutralizing effect on local acidification. Nitrate may act in the four ways proposed above. However, the possibility of sequestration of protons is limited by the large dissociation constant of  $\text{HNO}_3$  (Table 4). Phosphate ion may also act in the four ways, but it is expected to be more efficient as a pH buffer. However, if only  $\text{p}K_a$  values are considered carbonate ion should be more efficient than phosphate (Table 4), whereas the contrary is observed. The inhibiting efficiencies of the organic acids are not clearly associated with their dissociation constants, nor to their buffer capacities or to their molecular sizes (Carranza et al., 2008). In addition to considering the different ways in which an inhibitor may act, it is necessary to quantify the strength of these effects to predict its efficiency.

An anodic inhibitor of the localized corrosion must act over the anodic local kinetics. The localized acidification model introduces Eq. (12) for describing the contributions which made up the critical potential. The model accounts for steady state propagation of localized corrosion (Galvele, 1976, 1981; Gravano & Galvele, 1984).  $E_{\text{CORR}}^*$  is the corrosion potential in the local solution,  $\eta$  is the polarization needed for sustaining the critical chemistry ( $x \cdot i$ ),  $\Delta\Phi$  is the ohmic drop, and  $E_{\text{INH}}$  is the contribution to the polarization due to inhibitors (Galvele, 1976).

$$E_{\text{CRIT}} = E_{\text{CORR}}^* + \eta + \Delta\Phi + E_{\text{INH}} \quad (12)$$

Eq. (12) states the obvious fact that an inhibitor must produce an increase of  $E_c$  to act efficiently. Although the term  $E_{\text{INH}}$  accounts for the effects of inhibitors, it cannot be experimentally separated from the other contributions (Keitelman et al., 1984). Galvele (1976) states that the addition of  $\text{OH}^-$  or anions of weak acids increases the critical value of  $x \cdot i$ , which produces an increase of  $\eta$ . This effect is illustrated in Figure 5. However, the mass transport equations set by the model



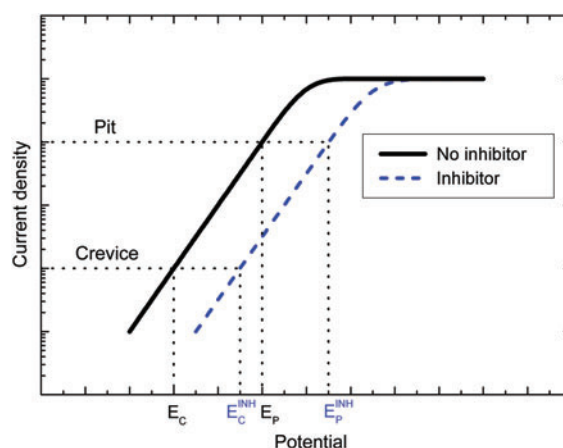
**Figure 5** Polarization curve of the alloy in the pit/crevice solution showing the effect of increasing the critical value of  $x \cdot i$  on the polarization contribution to  $E_{\text{CRIT}}$ .  $E_{\text{CRIT}}^{\text{INH}}$  is the critical potential in the presence of an inhibitor.

have not been solved for the concentrated solutions developed within pits and crevices of stainless alloys. In the context of the localized acidification model, it is proposed that an inhibitor should act by increasing any of the contributions to the critical potential:

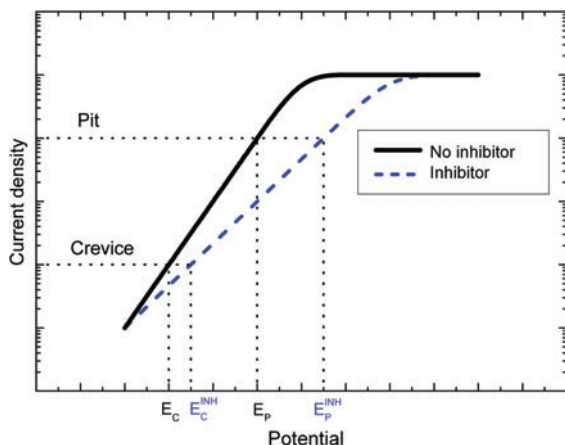
- Increasing  $E_{\text{CORR}}^*$  by increasing the oxidizing strength of the solution. It may be the case for nitrate, chromate, molybdate, perchlorate, and phosphate ions.
- Increasing  $\eta$  by increasing the polarization needed to sustain the critical chemistry ( $x \cdot i$ ) or by increasing the critical value of  $x \cdot i$  (Galvele, 1976). Most of the inhibitors may act in this way with a wide variety of effectiveness.
- Increasing  $\Delta\Phi$  by forming a more resistive salt film on the alloy surface. It may be the case for nitrate and phosphate ions, among others (Newman & Ajjawi, 1986; Yashiro et al. 1997). Increasing the critical value of  $x \cdot i$  leads to an indirect increase of  $\Delta\Phi$ .

Complete inhibition ( $R_{\text{CRIT}}$ ) is reached when critical chemistry is unable to be developed at any potential. This also depends on the geometrical conditions ( $x$ ). The inhibitors modify the polarization curve of the alloy in the pit/crevice by suppressing the anodic current to avoid the development of critical chemistry.

Figure 6 shows the effect of increasing  $E_{\text{CORR}}^*$  by the displacement of the polarization curve of the alloy in the pit/crevice solution. The increase of  $E_{\text{CORR}}^*$  is both effective at increasing the critical potentials of pitting and crevice corrosion. However, the increase of  $E_{\text{CORR}}^*$  may not only be caused by the displacement of the anodic curve on the noble direction but also by the increase of the rate of cathodic reactions within the crevice. In the latter case, the anodic curve is not necessarily modified. Figures 7 and 8 show the effect of increasing  $\eta$  and  $\Delta\Phi$ , respectively, on the polarization curve of the alloy in the pit/crevice solution. The increases of  $\eta$  and  $\Delta\Phi$  have a significant effect on pitting corrosion, but they



**Figure 6** Effect of increasing  $E_{\text{CORR}}^*$  on the polarization curve of the alloy in the pit/crevice solution.  $E_p^{\text{INH}}$  and  $E_c^{\text{INH}}$  are the critical potentials for pitting and crevice corrosion, respectively, in the presence of an inhibitor.

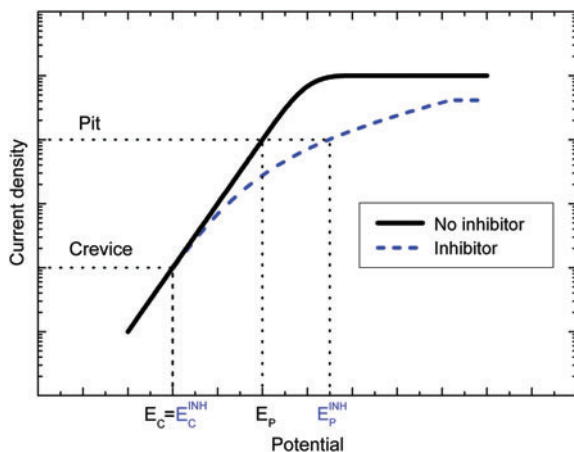


**Figure 7** Effect of increasing  $\eta$  on the polarization curve of the alloy in the pit/crevice solution.

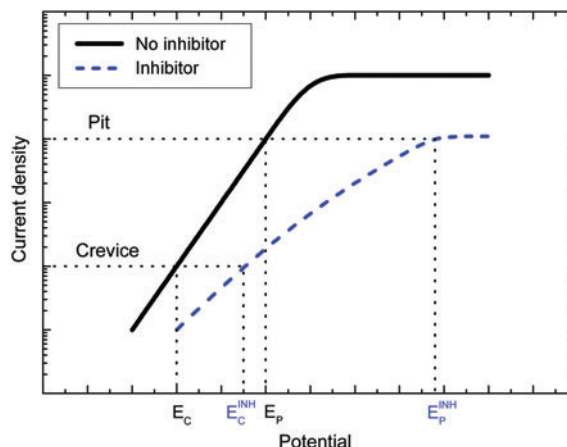
may not significantly affect crevice corrosion, as it proceeds at lower current densities. This distinction may explain why the effect of most of the inhibitors on crevice corrosion is generally slight or nil below  $R_{CRIT}$  (Figures 2 and 3). Figure 9 shows the effect of an inhibitor increasing the three contributions at the same time.

## 8. Future research needed

The study of the mechanisms of localized corrosion of stainless alloys and its inhibition is complicated by the fact that a very concentrated solution with a wide variety of dissolved anions is locally formed inside the pit/crevice. The successful models used to describe the localized corrosion of pure metals assume properties of diluted solutions (Tables 2 and 4) (Galvele, 1976, 1981; Gravano & Galvele, 1984). However, it should be noted that the approach is similar for both pure metals and corrosion resistant alloys. Stable localized corrosion



**Figure 8** Effect of increasing  $\Delta\Phi$  on the polarization curve of the alloy in the pit/crevice solution.



**Figure 9** Effects of increasing  $E_{CORR}^*$ ,  $\eta$ , and  $\Delta\Phi$  on the polarization curve of the alloy in the pit/crevice solution.

only proceeds when local dissolution at a certain rate is stabilized by a long enough diffusion path. Inhibitors act by reducing the rate of the local dissolution or avoiding its occurrence. A better understanding of the ion transport processes in concentrated multi-ionic solutions is still necessary. Interactions among alloying elements dissolved in the local solution and inhibitors entering the local environment from the bulk solution are needed to be understood. Effects of alloying elements and inhibitors are frequently assumed to be similar. Reliable databases with critical potentials and temperatures are also needed for validating any model to be developed (Anderko et al., 2004). A conjunction of experimental and theoretical work will be necessary to improve the present knowledge on inhibition of the localized corrosion of stainless alloys.

In the particular case of crevice corrosion, it should be taken into account that not all crevices have the same severity (Carranza et al., 2007; Giordano, Rincón Ortíz, Rodríguez, Carranza, & Rebak, 2011). In laboratory tests, crevices obtained by ceramic crevice formers wrapped with thick Polytetrafluoroethylene (PTFE) tape are more severe than those produced by solid PTFE material. The former leads to lower values of  $E_{RC}$  than the latter, especially in nonaggressive conditions (e.g., in the presence of inhibitors). The values of  $E_{RC}$  in the presence of inhibitors may be also affected by the technique used for determining  $E_{RC}$  (Giordano et al., 2011).  $E_{RC}$  obtained in the laboratory may be very conservative for industrial applications. The crevice severity for laboratory testing is the highest possible one, whereas in practical cases the crevice severity is unknown. Characterization of crevices in practical applications remains to be studied in detail.

## 9. Summary

The application of SS and chromium containing nickel-based alloys is limited by their susceptibility to localized corrosion. Inhibitors may be normally found in service environments or added on purpose to mitigate or avoid the effects of aggressive

agents such as chloride ions. Localized corrosion in the form of pitting and crevice corrosion may be inhibited by the additions of organic and inorganic inhibitors, surface treatments or by UV illumination.

Stable localized corrosion of stainless alloys occurs when the local dissolution is stabilized by a long enough diffusion path. The local chemistry of pits and crevices of stainless alloys is characterized by a low pH and a high chloride concentration. Inhibitors may act in one or more of the stages of the localized corrosion, such as pit nucleation, metastable pitting, and stable pitting propagation. They should reduce the rate of the local dissolution or avoid its occurrence.

The inhibitor efficiency depends on many factors, such as the alloy composition, surface treatment, potential range, aggressive anion identity and concentration, solution pH, temperature, etc. Pitting and crevice corrosion are the same phenomenon from an electrochemical viewpoint. Consequently, the effective inhibitors for the chloride induced pitting corrosion of stainless steels are equally effective for the crevice corrosion of the more corrosion resistant chromium containing nickel alloys.

Transport processes such as ion migration and diffusion are the key to describe the mechanisms of localized corrosion and its inhibition. Ion adsorption, pH buffering, metal salt precipitation, and transport mechanisms within these salts remain to be better understood for a proper description of localized corrosion. This study is complicated by the fact that very concentrated solutions with a wide variety of dissolved anions are formed.

It is proposed that an inhibitor should act by increasing any of the contributions to the critical potential: the corrosion potential in the local solution, the polarization needed for sustaining the critical chemistry, and the ohmic drop.

## Acknowledgments

Dr. R.M. Carranza is acknowledged for his useful comments and corrections to the original manuscript. Financial support from University of San Martín, Argentina (Grant SJ10/06) is acknowledged.

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Received June 6, 2011; accepted October 6, 2011