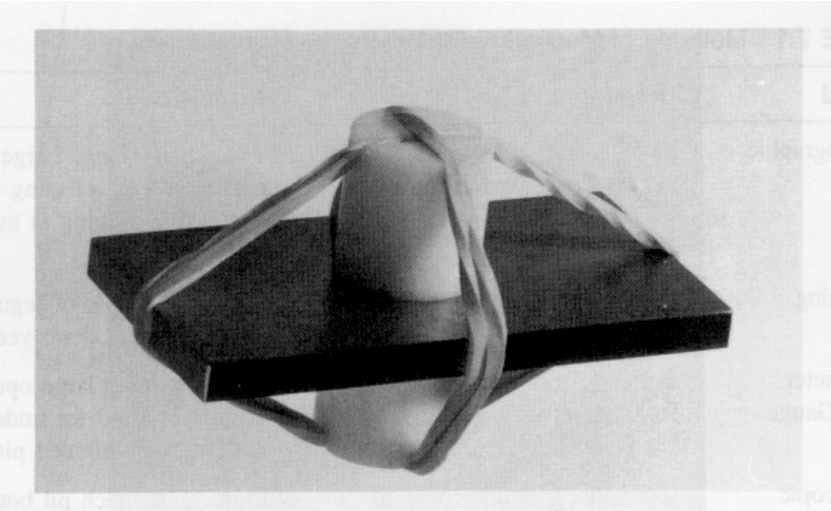
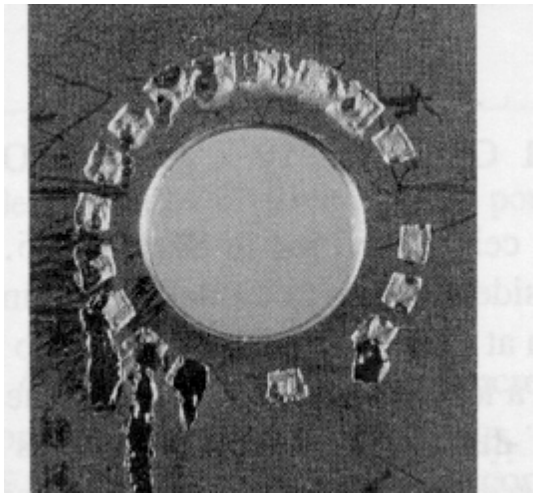
11. Crevice Corrosion

A localized corrosion occurs in crevices due to different environmental conditions. Crevice corrosion usually occurs within narrow fissures between metal/metal or metal/non metal joints such as flanges, gaskets, bolts, or even under deposits, due to limitation of the diffusion and migration of solution species to and from the bulk (outside) electrolyte through the small crevice gap.



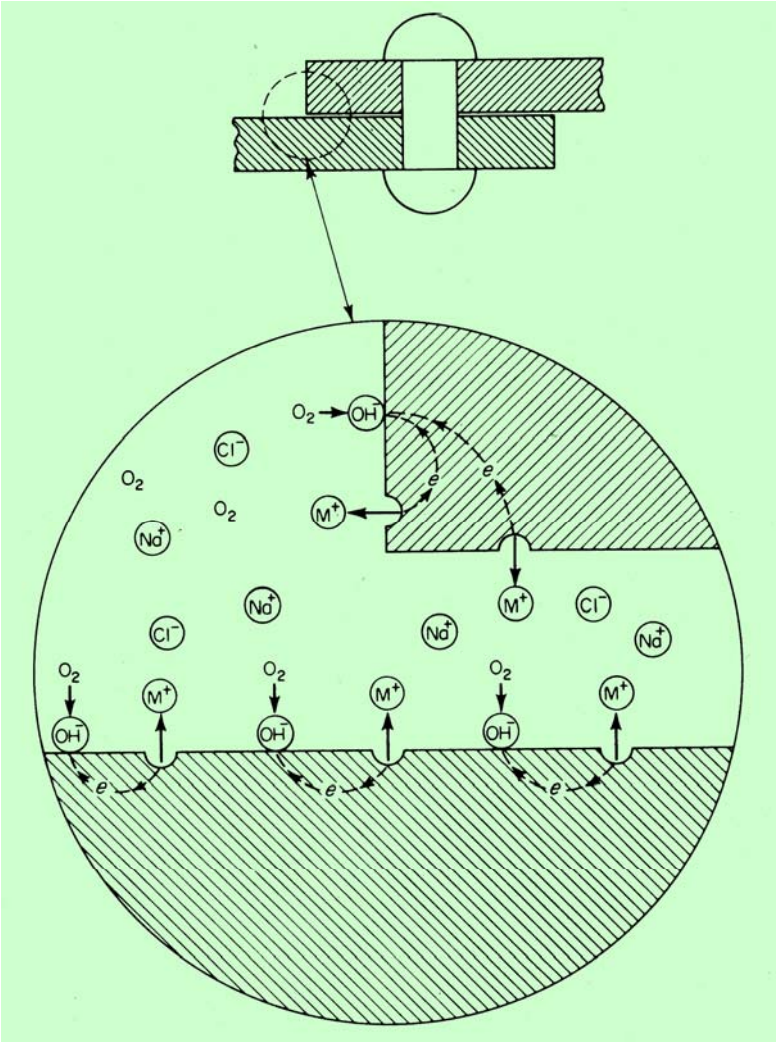
• **Crevice corrosion test assembly**

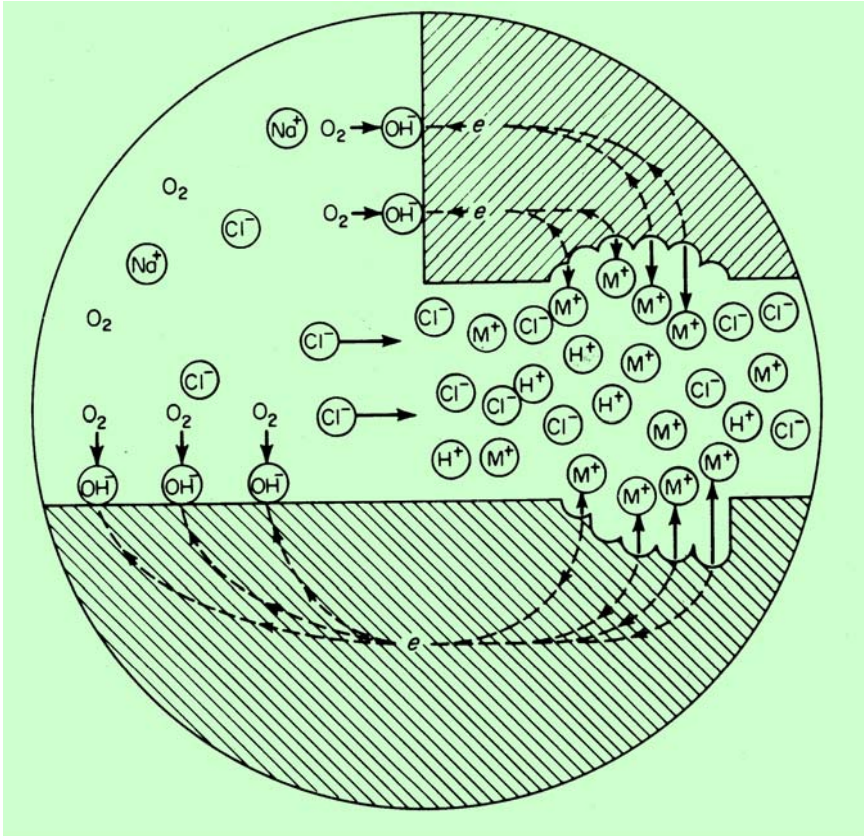


• **Crevice attack under serrated washers – type 304 stainless steel**

11.1 Mechanism of crevice corrosion

Consider a riveted plated section of metal M immersed in aerated sea water.





1) Initially, the following anodic and cathodic reactions occurs uniformly on the entire metal surface, inside and outside the crevice ;

Anodic reaction : $M \rightarrow M^{z+} + ze^-$
Cathodic reaction : $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$

2) After an induction period, O_2 in crevice is used up due to restricted convection ;

Crevice $\rightarrow$ low O_2 region $\rightarrow$ low E_a $\rightarrow$ small anode.
External surface $\rightarrow$ high O_2 region $\rightarrow$ high E_c $\rightarrow$ large cathode

3) Electromigration of Cl^- due to $\Delta E = E_a - E_c$

Anodic reaction in crevice : $M \rightarrow M^{z+} + e^-$

Excess positive charge(M^{z+}) is building up, which is balanced by the electromigration of Cl^- and other anions from outside.

• Anion migration : Anions such as Cl^-, OH^-, CO_3^{2-}, and SO_4^{2-} diffuse into the crevice with a velocity depending on its diffusion rate. Among the anions, Cl^- ion is the most fast.

• Cation migration : the metal ions accumulated in the crevice are transported slowly out of the crevice by diffusion and electromigration.

4) Acidification by hydrolysis reaction of metal ion ;

The abundance of metal ions inside the crevice gives rise to their hydrolysis with water molecules;

$M^{z+} + H_2O \rightarrow M(OH)_z\downarrow + z\ H^+$..... This reduces pH in the crevice. The low pH or acidity prevents passivation and facilitates anodic dissolution.

Table 5.2 Expressions for limiting pH of hydrolysis reaction mechanisms

Reaction	Equilibrium pH	pH of One Normal Solution
$Fe^{2+} + H_2O \rightarrow FeOH^+ + H^+$	$pH = 4.75 - 1/2 \log [Fe^{2+}]$	4.75
$Fe^{2+} + 2H_2O \rightarrow Fe(OH)_2 + 2H^+$	$pH = 6.64 - 1/2 \log [Fe^{2+}]$	6.64
$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3 + 3H^+$	$pH = 1.61 - 1/3 \log [Fe^{3+}]$	1.61
$Fe^{3+} + 2H_2O \rightarrow Fe(OH)_2^+ + 2H^+$	$pH = 2.00 - 1/3 \ln [Fe^{3+}]$	2.00
$2Fe^{3+} + 2H_2O \rightarrow Fe_2(OH)_2^{4+} + 2H^+$	$pH = 0.71 - 1/2 \ln [Fe^{3+}]$	0.71
$Fe^{3+} + H_2O \rightarrow FeOH^{2+} + H^+$	$pH = 1.52 - 1/2 \log [Fe^{3+}]$	1.52
$Cr^{2+} + 2H_2O \rightarrow Cr(OH)_2 + 2H^+$	$pH = 5.50 - 1/2 \log [Cr^{2+}]$	5.50
$Cr^{3+} + 3H_2O \rightarrow Cr(OH)_3 + 3H^+$	$pH = 1.60 - 1/3 \log [Cr^{3+}]$	1.60
$Ni^{2+} + 2H_2O \rightarrow Ni(OH)_2 + 2H^+$	$pH = 6.09 - 1/2 \log [Ni^{2+}]$	6.09

Table 10.1 Hydrolysis reactions and equilibrium pHs for metal ions in an occluded cell in stainless steels.

* In the case of pure metals, the pH values were found to be lower than those calculated from the metal ion conc., and the experimentally determined pHs were as follows ;

Fe :4.71, Cr :0.09, Ni :2.93, Mo :0.02, which indicates that Cr and Mo in an alloy would have the greatest effect in lowering the pH within the crevice or pit.

	304L *Fe-18Cr-10Ni*	**316L** *Fe-17Cr-13.7Ni-2.4Mo*	*Fe-18Cr-16Ni-5Mo*
pH	0.6 to 0.8	0.06 to 0.17	0.13 to 0.08
Cl^- conc. (N)	3.87	6.47	6.20
potential (V_{SCE})	-0.25 to -0.021	-0.02 to -0.22	-0.18 to -0.20

Table 10.2 pH, Cl^- and potential for artificial pits in stainless steels.

5) Depassivation

Passivation does not occur in the crevice when the critical pH and [Cl^-] in electrolyte of crevice have been achieved.

6) Cathodic protection of external surface

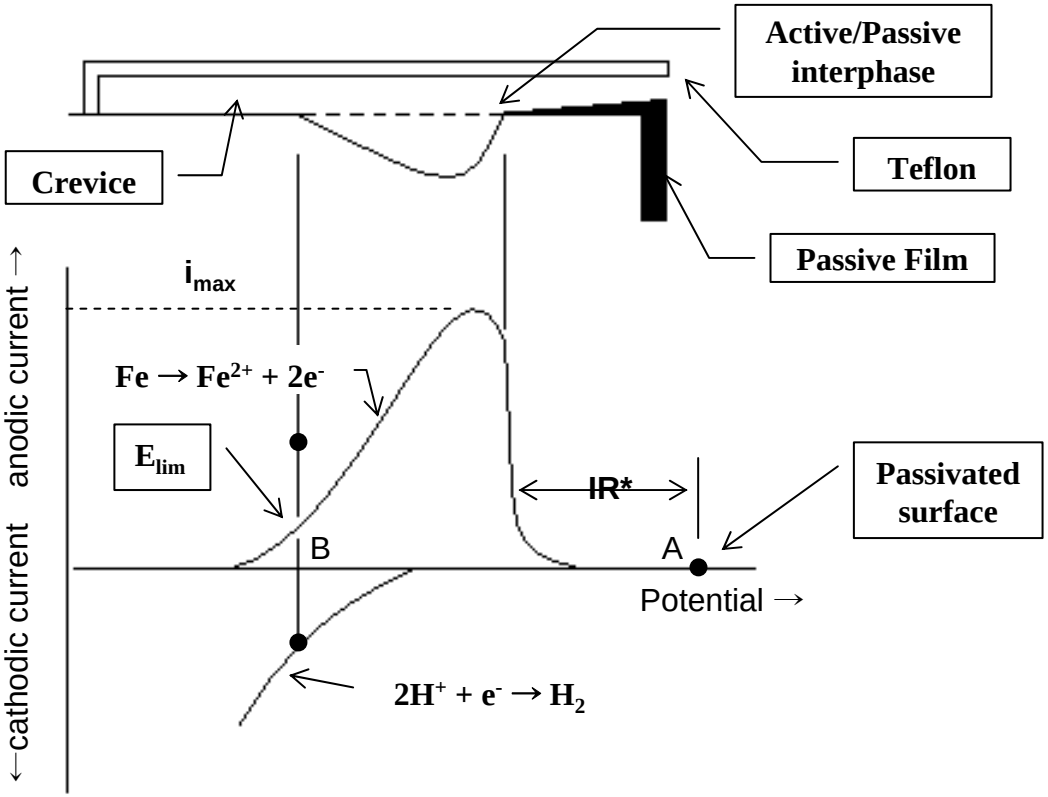
Cathodic reaction at external surface : $O_2 + 4H_2O + 4e^- \rightarrow 4OH^-$ .....High pH facilitates passivation of external surface and the external surface is cathodically protected by the electrons liberated by the anodic reaction.

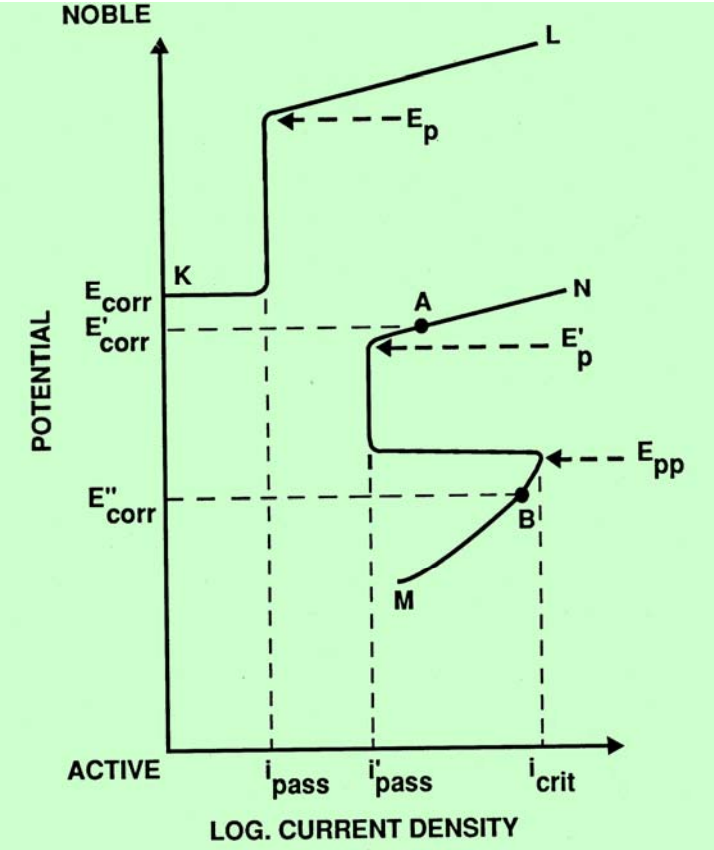
7) IR drop through passive film on external surface and along long and narrow electrolyte path between crevice and external surface maintains potential difference required to keep actively corroding in the crevice.

Low pH, high [Cl^-], depassivation, and IR drop lead to an accelerating or autocatalytic corrosion in the crevice.

11.2 *IR* voltage drop theory

The *IR* theory relates crevice corrosion to the shift with distance *x* on the wall of electrode potential, *E(x)*, into the active region of the polarization curve, thereby stabilizing the localized corrosion process. The change in composition of the crevice solution can promote the susceptibility to crevice corrosion by the IR mechanism through its effect on increasing the active and passive currents of the system's polarization curve.





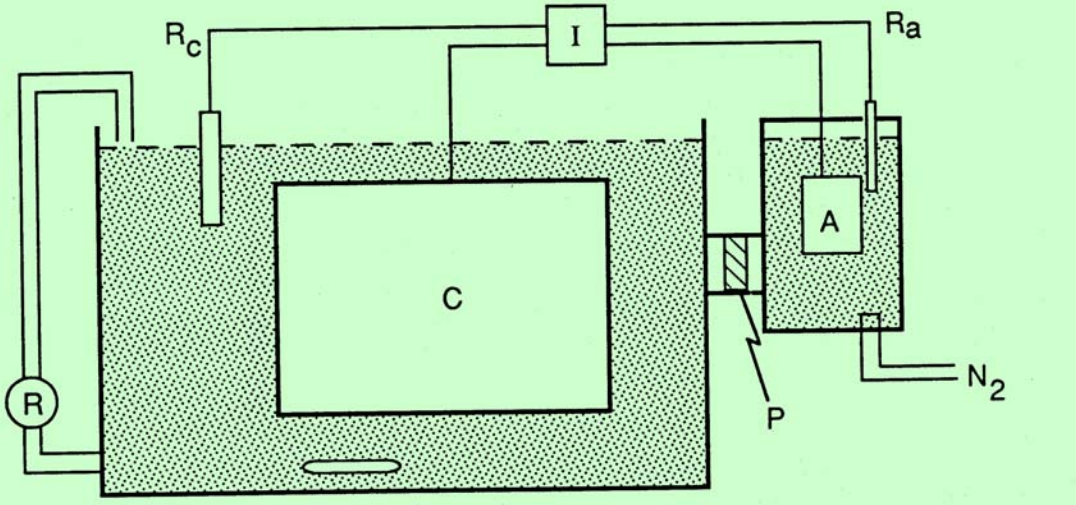


Figure 5.16 A schematic layout identifying various components of the compartmentalized cell used in crevice corrosion research. (After Reference 52.) *A* = Anode; *C* = cathode; R_a, R_c = reference electrodes; *P* = cell partition; *I* = instrumentation; *R* = recirculation pump/reservoir.

$A_a : A_c = 1 : 37$

11.3 Prevention of crevice corrosion

1) Use welded parts.
2) Design vessels for complete drainage.
3) keep process solution clean.
4) Inspect equipment and remove deposits frequently.
5) Remove solids in suspension early in the process.