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Diagnosis and Management of Adverse Reactions to Metal Debris

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Abstract

Modern total hip arthroplasty implants have incorporated modularity into their designs, providing the benefits of intraoperative flexibility and the ability to exchange the femoral heads in the future if necessary. However, this feature has unfortunately predisposed patients to the effects of corrosion, potentially resulting in adverse local tissue reactions (ALTR) and even systemic effects. A thorough understanding of the science of corrosion is important for the treating surgeon so that they can understand the underlying pathology, quickly diagnose the condition of ALTR, and risk stratify their patients to determine the best method of treatment. Revision surgery is not always necessary in cases of trunnionosis or ALTR, but the results of revision surgery are generally favorable.

Keywords

Corrosion; total hip arthroplasty; trunnionosis; adverse local tissue reaction; revision surgery

Introduction

Since the late 1980s, modularity in total hip arthroplasty has become increasingly prevalent.^{1,2} Initially, modular femoral heads were introduced, providing the benefits of intraoperative flexibility and the ability to exchange the femoral heads in the future if necessary.³⁻⁵ Following this, femoral stems with modular connections between the neck and body of the stem were introduced, allowing for adjustments in version, offset, and length separate from femoral stem fixation.^{6,7} The introduction of these components brought about concerns regarding metal corrosion at the modular connections.^{8,9} These concerns were corroborated in the early 1990's by reports of fretting, crevice, and galvanic corrosion that were observed in retrieved hip implants.¹⁰ Additionally, soft tissue reactions from the corrosion, currently labeled adverse local tissue reaction (ALTR), began to be linked to head-neck trunnion corrosion.¹¹

Metal-on-metal (MoM) hip implants historically were associated with metal-related tissue necrosis and revision.¹² However, in an attempt to address concerns with conventional

polyethylene wear, MoM bearing use became more popular in the early- to mid-2000's. During this time, soft tissue reactions associated with metal resurfaced as a cause of implant failure with some arthroplasty models.^{13–16} Using varying diagnostic tools, multiple studies reported that metal-associated tissue destruction, which was originally believed to be exclusive to MoM implants, could similarly be detected in arthroplasty designs utilizing metal-on-polyethylene bearings.^{17–19} The extent that ALTR in MoM hip replacements is secondary to metal wear debris from modular taper junction corrosion or from the MoM articulation has yet to be determined.^{20,21}

Most modern total hip arthroplasty implants incorporate modularity into their designs, and it is essential that orthopedic surgeons recognize the process by which corrosion at these interfaces can affect implant outcomes. This article discusses the concepts of corrosion effects on implant surfaces, the way passive oxide layers insulate metal from corrosion, the varying categories of implant related corrosion, and how these interrelate at modular taper junctions to hasten corrosion and reduce implant performance. Furthermore, this article explores the corrosion associated complication of ALTR and provides insight into how to diagnose and manage this complication.

Corrosion Basic Science

The process of corrosion occurs from a material's inherent drive to reach a lower chemical energy state. This is accomplished through the flow of electrons from an anode towards a cathode, and it requires minimal activation energy. The reaction may be violently exothermic if a metal that does not possess an insulating metal-oxide layer is directly exposed to an aqueous solution or oxygen. To counter this violent exothermic reaction, orthopedic implants rely on a protective oxide film, also known as a passive layer, to provide protection against corrosion.

The process of corrosion may be divided into three steps, as seen in Figure 1. During the first phase, oxidation occurs as cations are removed when metal from a metal surface dissolves into an aqueous environment. Following this, reduction occurs when electrons are attracted to a differential charge at another location on the metal surface, and an electrical current is created as electrons are detached from the surface. Finally, byproducts, namely metal oxide or insoluble metal hydroxide, form a protective surface on the metal. This insulating surface forms through a process known as "passivation", and it hinders the kinetics of corrosion.²²

Orthopedic implants rely on the passive "chemically stable" metal oxide layer to inhibit the process of corrosion. In contrast to metal hydroxide, metal oxide provides more insulation as it has more stability and is less dissolvable. These properties inhibit the movement of ions from a solution's aqueous layer to the metal surface, reducing the degree of corrosion. It is important to note that these insulating surfaces can only develop with certain metal alloys, such as titanium, chromium, tantalum, niobium, and zirconium. Other metals such as aluminum, copper, lanthanide may develop metal oxide layers, however, these insulating films typically rapidly dissolve when exposed to chloride ions, which is a key component of

physiologic solutions. Metal hydroxide surfaces may also form from metal in alloys, but this has much less capability to inhibit corrosion due to its instability.

Although corrosion may still happen following passivation, the insulating layer acts as a kinetic barrier and decreases the rate of the corrosion process. Passivation affects the thermodynamics of the reaction by raising the activation energy required. The insulating layer develops rapidly on metal surfaces, and corrosion is prevented if the layer remains homogenous, allowing it to protect the surface of the metal from the aqueous solution, as seen in Figure 2. Insulating surfaces derive their ability to protect against corrosion because of their stability and their depth. The passive layers are dynamic, as the depth of the surface results from an equilibrium between processes that dissolve and those that develop the surface, and based upon the current crossing the layer and acidity of the adjacent aqueous solution.²³

Types of Corrosion

The commonly discussed categories of corrosion that may transpire on orthopedic implants comprise of pitting, crevice, frettings, and mechanically assisted crevice corrosion (MACC). These categories of corrosion can be thought of as a span that is dependent upon a metal alloy's capability to protect its shielding passive film from dissolving.

Pitting corrosion refers to corrosion from a contained disturbance in the insulating film, as seen in Figure 3. This disturbance in the protective layer results in a more suitable setting for corrosion by reducing the activation energy obstacle for corrosion and increasing the kinetics in that zone. Disturbances that form in the protective layer lead to the formation of an anode and isolated corrosion.²⁴ This may occur if one zone forms the more dissolvable hydroxide rather than the more stable oxide, rendering this area vulnerable to defects on the protective layer. Halides, such as chlorine, are plentiful in physiologic solutions that can lead to the dissolution of oxides. This permits a greater stream of metal ions to leak from this small disturbed zone in the protective layer. In response, a cathode may form over a sizeable distant area as a consequence of the development of a point anode, generating a potential charge that may result in current flow and ultimate galvanic corrosion.^{24,25}

Crevice corrosion, seen in Figure 4, refers to corrosion in a gapped area where there is restricted circulation of ions to and from the area, producing extremely corrosive conditions. These conditions result in the requirement of a lower activation energy to cause corrosion than that of pitting corrosion. With regards to orthopedic implants, the total hip arthroplasty trunnion represents a sealed setting that does not allow for ion circulation. In reality, there is only a limited seal at a distinct area on the neck-head taper link, rather than throughout the complete taper surface. The sealed portion of the trunnion does, however, hinder the circulation of ions and oxygen. This interferes with the ability of the protective layer to redevelop as oxygen is required to redevelop the metal oxide film. In addition, acidic conditions develop secondary to the high levels of hydrogen ions that hastens corrosion. Finally, the high levels of available chloride result in instability of the protective film and render it prone to dissolution. All of these factors result in the development of a non-uniform

protective layer that is unable to insulate the metal surface from the aqueous solution resulting in corrosion.

Fretting corrosion refers to mechanical wear of a metal that causes breakdown of the protective insulating layer. When this corrosion takes place within a crevice, as can be seen in Figure 5, the term mechanically assisted crevice corrosion (MACC) is used. Tribocorrosion is another term that is defined by the combination of wear and corrosion.^{26,27} Mechanical stresses interrupt the insulating later that protects the metal surface from corrosion. With regards to orthopedic implants, this occurs when minute movements amongst the taper surfaces may disrupt the protective layer, resulting in substantial fretting corrosion or MACC.

Trunnion Corrosion

With regards to the total hip arthroplasty trunnion, multiple features may affect the stability of the protective layer. One of these features is the gradient in which the taper surfaces exists in relation to the long axis of the implant.²⁸ Multiple other features of the taper structure, including the elastic modulus of the metal, contribute to the structural rigidity. Several studies have demonstrated that other factors that affect structural rigidity, such as smaller diameter trunnions and shorter taper length, are key parameters that result in trunnion corrosion.^{29–33} Despite this, the effect that these difference design parameters contribute towards susceptibility of an implant to corrosion *in vivo* settings is unclear.

In addition, the amount of mechanical forces through the trunnion may also affect the ability of the protective film to resist corrosion. For example, femoral heads with greater diameters likely have more physical distortion at the taper junction and an increased amount of movement amongst the mating surfaces. This theoretical concern has been demonstrated clinically in reports that have demonstrated that femoral heads with greater diameters are linked to the development of ALTR.^{34–36} It is commonly acknowledged that greater amounts of mechanical forces and motion across the trunnion secondary to differing model designs causes corrosion and subsequent ALTR.

Diagnosis of ALTR

Patients may present with symptomatic ALTR at various timepoints after a total hip arthroplasty. While large cohort studies suggest that the mean time to presentation is approximately 4 years following total hip arthroplasty⁸, there are reports of patients presenting with ALTR within the first year or up to several decades following the index procedure.¹⁸

The most common clinical presentation of a patient with ALTR is pain in or around the peritrochanteric region, the buttock, thigh, or the groin. Although, many cases of ALTR may be asymptomatic³⁷, patients may also present with palpable fluid collections near the hip, and others may exhibit a limp secondary to muscle weakness.⁸ A small subset of patients with ALTR may also demonstrate symptoms of hip instability without the presence of baseline pain. Consequentially, ALTR secondary to trunnion corrosion must be a component of the differential diagnosis of patients presenting with recurrent instability in the absence of

other clear causes. Evaluation of serum metal levels commonly reveals cobalt and chromium levels above reference values, with a greater magnitude of serum cobalt elevation in comparison to chromium.³⁸

It is essential that prosthetic joint infection (PJI) is ruled out in the differential diagnosis when addressing patients suspected to have developed ALTR. This may be difficult as PJI and ALTR may both present with similar symptoms, such as pain, fluid collections, and elevated inflammatory marker. In addition, it may be problematic to obtain an accurate cell count in the presence of clumped cells and metal debris.³⁸ Despite these challenges, there are still validated methods to help the treating surgeon distinguish between ALTR and PJI. While inflammatory markers have been demonstrated to be elevated in approximately half of patients with ALTR, using cutoff values of ESR = 32 mm/hr and CRP = 10.0 mg/L have been reported to be effective in distinguishing between PJI and ALTR.³⁹ With regards to synovial fluid analysis, it has been reported that up to one-third of samples may be inadequate for analysis secondary to the presence of clots, fragmented cells, and amorphous material. However, when adequate samples are obtained, cutoff values of WBC = 4350 WBC/ μ L and differential of 85% polymorphonucleocytes have been demonstrated to have high diagnostic utility.³⁹

With regards to imaging, initial evaluation generally involves obtaining plain radiographs. While radiographs may detect other causes of painful hips in the context of total hip arthroplasty such as component loosening, periprosthetic fracture, or component malpositioning, ALTR generally does not present with radiographic findings.³⁸ For this reason, advanced imaging is generally recommended to further workup a differential diagnosis that includes ALTR. Computed tomography, ultrasound, and MRI have all been proposed to have advantages and disadvantages for imaging potential ALTR.⁴⁰ However, metal-artifact reduction sequencing MRI has been demonstrated to have high sensitivity and ability to detect tissue damage, and thus is the imaging modality of choice when working up a potential diagnosis of ALTR.³⁸

Management of ALTR

Patients who develop pain in the context of soft tissue damage from ALTR typically require revision surgery to address the damaged tissue and to prevent further corrosion and progressive damage. Early surgical treatment is supported by studies that have demonstrated more severe soft tissue damage in patients with longer durations between presentation with ALTR and surgical treatment.⁴¹ However, in patients with a painless total hip arthroplasty with evidence of pseudotumor, management may be dictated by risk-stratification as described by Kwon *et al.* This stratification system is based upon patient symptoms, clinical exam, femoral implant modularity type, radiographs, inflammatory markers, metal ion levels, and cross-sectional imaging. Patient's who fall into the low risk group may undergo continued observation with routine annual follow-up. Those in the moderate risk group should be considered for revision surgery if symptoms or imaging abnormalities progress, or if rising metal ion levels are noted over a course of six months. Finally, the patients in the high-risk category should be considered for revision surgery at the time of presentation.

However, if they elect to decline surgery they should be followed at six-month intervals, similar to those in the moderate risk category.⁴²

Studies have demonstrated that the trunnion's integrity is preserved in most instances of head-neck junction corrosion.⁸ Therefore, generally the standard of care for treating ALTR involves replacement of the femoral head without removal of the femoral stem. This has been supported by evidence revealing that a femoral head replacement on a corroded trunnion with no gross visible volume loss is not linked to poor outcomes or early failure.⁴³ To prevent additional corrosion and eliminate one source of chromium and cobalt, it is recommended that the femoral head is replaced with a ceramic head on a titanium sleeve.⁴⁴ It is possible that older arthroplasty designs do not allow for placement of a ceramic head. In these situations, the producer of the implant can potentially provide a custom head. If this is not feasible, a metal head can be utilized, but this is not ideal and may predispose the patient to recurrent ALTR.¹⁸

Following revision surgery for ALTR, patients have acceptable results. It has been noted that cobalt and chrome levels decrease quickly following surgery.¹⁸ In addition, patients generally demonstrate an improvement as based upon Harris Hip Scores.⁸ Despite these typical results, patients who undergo revision surgery for ALTR are at increased risk of complications, such as sciatic nerve palsy, instability, and infection. Of these, instability is the most frequent complication, potentially due to muscle injury from the ALTR or the debridement to address the condition. As a result, some patients do go onto a second revision surgery with a liner exchange to a constrained liner.⁴⁵

Conclusion

The incorporation of modularity into modern total hip arthroplasty designs has brought many benefits to physicians and patients alike, however, it has also predisposed patients to the effects of corrosion at the modular interfaces. A thorough understanding of the science of corrosion is important for the treating surgeon so that they can understand the underlying pathology and risk stratify their patients to determine treatment. Revision surgery is not always necessary in cases of trunnionosis or ALTR, but the results of revision surgery are generally favorable.

References

1. Kop AM, Swarts E. 2009 Corrosion of a hip stem with a modular neck taper junction: a retrieval study of 16 cases. *J. Arthroplasty* 24(7):1019–1023. [PubMed: 18835686]
2. Collier JP, Surprenant VA, Jensen RE, Mayor MB. 1991 Corrosion at the interface of cobalt-alloy heads on titanium-alloy stems. *Clin. Orthop. Relat. Res* (271):305–312.
3. Jacobs JJ, Urban RM, Gilbert JL, et al. 1995 Local and distant products from modularity. *Clin. Orthop. Relat. Res* (319):94–105. [PubMed: 7554654]
4. Collier JP, Mayor MB, Williams IR, et al. 1995 The tradeoffs associated with modular hip prostheses. *Clin. Orthop. Relat. Res* (311):91–101.
5. Cook SD, Barrack RL, Baffes GC, et al. 1994 Wear and corrosion of modular interfaces in total hip replacements. *Clin. Orthop. Relat. Res* (298):80–88.
6. Duwelius PJ, Hartzband MA, Burkhart R, et al. 2010 Clinical results of a modular neck hip system: hitting the "bull's-eye" more accurately. *Am. J. Orthop. (Belle Mead, NJ)* 39(10 Suppl):2–6.

7. Archibeck MJ, Cummins T, Carothers J, et al. 2011 A comparison of two implant systems in restoration of hip geometry in arthroplasty. *Clin. Orthop. Relat. Res* 469(2):443–446. [PubMed: 21082363]
8. Cooper HJ, Della Valle CJ, Berger RA, et al. 2012 Corrosion at the head-neck taper as a cause for adverse local tissue reactions after total hip arthroplasty. *J. Bone Joint Surg. Am* 94(18):1655. [PubMed: 23289127]
9. Mao X, Tay GH, Godbolt DB, Crawford RW. 2012 Pseudotumor in a well-fixed metal-on-polyethylene uncemented hip arthroplasty. *J. Arthroplasty* 27(3):493–e13.
10. Gilbert JL, Buckley CA, Jacobs JJ. 1993 In vivo corrosion of modular hip prosthesis components in mixed and similar metal combinations. The effect of crevice, stress, motion, and alloy coupling. *J. Biomed. Mater. Res* 27(12):1533–1544. [PubMed: 8113241]
11. Svensson O, Mathiesen EB, Reinholt FP, Blomgren G. 1988 Formation of a fulminant soft-tissue pseudotumor after uncemented hip arthroplasty. A case report. *JBJS* 70(8):1238–1242.
12. Evans EM, Freeman MAR, Miller AJ, Vernon-Roberts B. 1974 Metal sensitivity as a cause of bone necrosis and loosening of the prosthesis in total joint replacement. *J. Bone Joint Surg. Br* 56(4):626–642. [PubMed: 4452710]
13. Clayton RAE, Beggs I, Salter DM, et al. 2008 Inflammatory pseudotumor associated with femoral nerve palsy following metal-on-metal resurfacing of the hip: a case report. *JBJS* 90(9):1988–1993.
14. Counsell A, Heasley R, Arumilli B, Paul A. 2008 A groin mass caused by metal particle debris after hip resurfacing. *Acta Orthop. Belg* 74(6):870. [PubMed: 19205339]
15. Mahendra G, Pandit H, Kliskey K, et al. 2009 Necrotic and inflammatory changes in metal-on-metal resurfacing hip arthroplasties: relation to implant failure and pseudotumor formation. *Acta Orthop* 80(6):653–659. [PubMed: 19995315]
16. Campbell P, Ebrahimzadeh E, Nelson S, et al. 2010 Histological features of pseudotumor-like tissues from metal-on-metal hips. *Clin. Orthop. Relat. Res* 468(9):2321–2327. [PubMed: 20458645]
17. Fricka KB, Ho H, Peace WJ, Engh CA Jr. 2012 Metal-on-metal local tissue reaction is associated with corrosion of the head taper junction. *J. Arthroplasty* 27(8):26–31. [PubMed: 22554728]
18. Plummer DR, Berger RA, Paprosky WG, et al. 2016 Diagnosis and management of adverse local tissue reactions secondary to corrosion at the head-neck junction in patients with metal on polyethylene bearings. *J. Arthroplasty* 31(1):264–268.
19. Urish KL, Hamlin BR, Plakseychuk AY, et al. 2017 Trunnion failure of the recalled low friction ion treatment cobalt chromium alloy femoral head. *J. Arthroplasty* 32(9):2857–2863. [PubMed: 28478184]
20. Cook RB, Bolland BJRF, Wharton JA, et al. 2013 Pseudotumour formation due to tribocorrosion at the taper interface of large diameter metal on polymer modular total hip replacements. *J. Arthroplasty* 28(8):1430–1436. [PubMed: 23528556]
21. Jacobs JJ, Cooper HJ, Urban RM, et al. 2014 What do we know about taper corrosion in total hip arthroplasty? *J. Arthroplasty* 29(4):668–669. [PubMed: 24655613]
22. Jacobs JJ, Gilbert JL, Urban RM. 1998 Corrosion of metal orthopaedic implants. *Jbjs* 80(2):268–282.
23. Macdonald DD. 2011 The history of the point defect model for the passive state: a brief review of film growth aspects. *Electrochim. Acta* 56(4):1761–1772.
24. Szklarska-Smialowska Z 1986 Pitting corrosion of metals.
25. Hodgson AW, Mischler S, Von Rechenberg B, Virtanen S. 2007 An analysis of the in vivo deterioration of Co-Cr-Mo implants through wear and corrosion. *Proc. Inst. Mech. Eng. Part H J. Eng. Med* 221(3):291–303.
26. Wimmer MA, Fischer A, Büscher R, et al. 2010 Wear mechanisms in metal-on-metal bearings: The importance of tribochemical reaction layers. *J. Orthop. Res* 28(4):436–443. [PubMed: 19877285]
27. Muñoz AI, Mischler S. 2007 Interactive effects of albumin and phosphate ions on the corrosion of CoCrMo implant alloy. *J. Electrochem. Soc* 154(10):C562–C570.
28. Lucas LC, Buchanan RA, Lemons JE. 1981 Investigations on the galvanic corrosion of multialloy total hip prostheses. *J. Biomed. Mater. Res* 15(5):731–747. [PubMed: 12659138]

29. Brown SA, Flemming CAC, Kawalec JS, et al. 1995 Fretting corrosion accelerates crevice corrosion of modular hip tapers. *J. Appl. Biomater* 6(1):19–26. [PubMed: 7703534]
30. Goldberg JR, Gilbert JL, Jacobs JJ, et al. 2002 A multicenter retrieval study of the taper interfaces of modular hip prostheses. *Clin. Orthop. Relat. Res* 401:149–161.
31. Grupp TM, Weik T, Bloemer W, Knaebel H-P. 2010 Modular titanium alloy neck adapter failures in hip replacement-failure mode analysis and influence of implant material. *BMC Musculoskelet. Disord* 11(1):3. [PubMed: 20047653]
32. Brock TM, Sidaginamale R, Rushton S, et al. 2015 Shorter, rough trunnion surfaces are associated with higher taper wear rates than longer, smooth trunnion surfaces in a contemporary large head metal-on-metal total hip arthroplasty system. *J. Orthop. Res* 33(12):1868–1874. [PubMed: 26135357]
33. Nassif NA, Nawabi DH, Stoner K, et al. 2014 Taper design affects failure of large-head metal-on-metal total hip replacements. *Clin. Orthop. Relat. Res* 472(2):564–571. [PubMed: 23801060]
34. Bishop N, Witt F, Pourzal R, et al. 2013 Wear patterns of taper connections in retrieved large diameter metal-on-metal bearings. *J. Orthop. Res* 31(7):1116–1122. [PubMed: 23440943]
35. Bolland B, Culliford DJ, Langton DJ, et al. 2011 High failure rates with a large-diameter hybrid metal-on-metal total hip replacement: clinical, radiological and retrieval analysis. *J. Bone Joint Surg. Br* 93(5):608–615. [PubMed: 21511925]
36. Langton D, Ahmed I, Avery P, et al. 2017 Investigation of taper failure in a contemporary metal-on-metal hip arthroplasty system through examination of unused and explanted prostheses. *JBJS* 99(5):427–436.
37. Kwon Y-M, Khormae S, Liow MHL, et al. 2016 Asymptomatic pseudotumors in patients with taper corrosion of a dual-taper modular femoral stem: MARS-MRI and metal ion study. *JBJS* 98(20):1735–1740.
38. Cooper HJ. 2016 Diagnosis and treatment of adverse local tissue reactions at the head-neck junction. *J. Arthroplasty* 31(7):1381–1384. [PubMed: 27113943]
39. Paul HY, Cross MB, Moric M, et al. 2015 Do serologic and synovial tests help diagnose infection in revision hip arthroplasty with metal-on-metal bearings or corrosion? *Clin. Orthop. Relat. Res* 473(2):498–505. [PubMed: 25171935]
40. Nam D, Barrack RL, Potter HG. 2014 What are the advantages and disadvantages of imaging modalities to diagnose wear-related corrosion problems? *Clin. Orthop. Relat. Res* 472(12):3665–3673. [PubMed: 24664197]
41. McGrory BJ, MacKenzie J, Babikian G. 2015 A high prevalence of corrosion at the head–neck taper with contemporary Zimmer non-cemented femoral hip components. *J. Arthroplasty* 30(7):1265–1268. [PubMed: 25737386]
42. Kwon Y-M, Fehring TK, Lombardi AV, et al. 2014 Risk stratification algorithm for management of patients with dual modular taper total hip arthroplasty: consensus statement of the American Association of Hip and Knee Surgeons, the American Academy of Orthopaedic Surgeons and the Hip Society. *J. Arthroplasty* 29(11):2060–2064. [PubMed: 25189673]
43. Goyal N, Ho H, Fricka KB, Engh CA Jr. 2014 Do you have to remove a corroded femoral stem? *J. Arthroplasty* 29(9):139–142. [PubMed: 24973927]
44. Kurtz SM, Kocagöz SB, Hanzlik JA, et al. 2013 Do ceramic femoral heads reduce taper fretting corrosion in hip arthroplasty? A retrieval study. *Clin. Orthop. Relat. Res* 471(10):3270–3282. [PubMed: 23761174]
45. Lash NJ, Whitehouse MR, Greidanus NV, et al. 2016 Delayed dislocation following metal-on-polyethylene arthroplasty of the hip due to ‘silent’trunnion corrosion. *Bone Joint J* 98(2):187–193. [PubMed: 26850423]

Figure 1: The Basic Steps of Corrosion.

During the first phase (1), oxidation occurs as cations are removed when metal from a metal surface dissolves into an aqueous environment. Following this, reduction occurs when electrons are attracted to a differential charge at another location on the metal surface, and an electrical current is created as electrons are detached from the surface (2). Finally, byproducts, namely metal oxide or insoluble metal hydroxide, form a protective surface on the metal (3). This insulating surface forms through a process known as “passivation”, and it hinders the kinetics of corrosion. e^- , electrons; M , elemental metal; M^+ , cationic metal ion; OH^- , hydroxide ion; H_2O , water; O_2 , oxygen; H_2 , hydrogen; MO_2 , metal oxide; MOH , metal hydroxide.

Figure 2: Prevention of Corrosion by a Passive Metal Oxide Layer.

Passivation affects the thermodynamics of the reaction by raising the activation energy required. The insulating layer develops rapidly on metal surfaces, and corrosion is prevented if the layer remains homogenous, allowing it to protect the surface of the metal from the aqueous solution. Insulating surfaces derive their ability to protect against corrosion because of their stability and their depth. The passive layers are dynamic, as the depth of the surface results from an equilibrium between processes that dissolve and those that develop the surface and based upon the current crossing the layer and acidity of the adjacent aqueous solution. e^- electrons; M elemental metal; M^+ cationic metal ion; OH^- hydroxide ion; H_2O water; O_2 oxygen; H_2 hydrogen; MO metal oxide; MOH metal hydroxide.

Figure 3: Pitting corrosion.

Disturbances that form in the protective layer lead to the formation of an anode and isolated corrosion. This may occur if one zone forms the more dissolvable hydroxide rather than the more stable oxide, rendering this area vulnerable to defects on the protective layer. In response, a cathode may form over a sizeable distant area as a consequence of the development of a point anode, generating a potential charge that may result in current flow and ultimate galvanic corrosion. e^- electrons; M elemental metal; M^+ cationic metal ion; OH^- hydroxide ion; H_2O water; O_2 oxygen; H_2 hydrogen; MO_2 metal oxide; MOH metal hydroxide.

Figure 4: Crevice corrosion.

Crevice corrosion refers to corrosion in a gapped area where there is restricted circulation of ions to and from the area, producing extremely corrosive conditions. These conditions result in the requirement of a lower activation energy to cause corrosion than that of pitting corrosion. e^- electrons; M elemental metal; M^+ cationic metal ion; OH^- hydroxide ion; H_2O water; O_2 oxygen; H_2 hydrogen; MO_2 metal oxide; MOH metal hydroxide.

Figure 5: Fretting corrosion or MACC.

Fretting corrosion refers to mechanical wear of a metal that causes breakdown of the protective insulating layer. When this corrosion takes place within a crevice, the term mechanically assisted crevice corrosion (MACC) is used. e^- electrons; M elemental metal; M^+ cationic metal ion; OH^- hydroxide ion; H_2O water; O_2 oxygen; H_2 hydrogen; MO_2 metal oxide; MOH metal hydroxide.