

MECHANISM OF CORROSION-ENHANCED EROSION OF STEELS IN OIL AND GAS PRODUCTION

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Abstract

Challenges due to erosion-corrosion in oil and gas production are briefly reviewed. In accordance with theories of non-equilibrium thermodynamics, mechanical metallurgy and electrochemistry, the theoretical models were built to assess the synergistic effect in slurry erosion process. The new models have been validated by experiments to evaluate the hardness degradation induced by corrosion and the consequently accelerated erosion. The experimental investigations demonstrated that the corrosion-induced surface hardness degradation is governed by a mechanism of the corrosion-enhanced erosion of steels. The corrosion-induced erosion is also observable in flowing electrolyte free of solid particles. Based on the understanding of erosion-corrosion mechanisms, the methods to evaluate the erosion-corrosion resistance of materials and the approaches to mitigate the damage caused by erosion-corrosion are recommended.

Introduction

With a few exceptions, most metals owe their corrosion resistance to a protective surface film. Erosive fluids can damage the protective film, and remove small pieces of material as well, leading to a significant increase in penetration rate. The removal of the film by erosive slurry gives corrosion rates in the order of 10mm/y (400 mils/y) in addition to any erosion of underlying metal. The damage to the protect film may be the results of the fluid-induced mechanical forces or flowing-enhanced dissolution. Meanwhile, the corrosion can cause degradation in surface properties and promote the mechanical erosion under action of the mechanical forces [1]. This conjoint action of erosion and corrosion is known as erosion-corrosion. Erosion-corrosion encompasses a wide range of flow-induced corrosion. It is also regarded as a subject within the broader area of tribo-corrosion which covers all aspects of tribologically (mainly mechanically) induced interactions with electrochemical processes [2].

The mechanisms of flow accelerated corrosion relate to the destructing and reforming of protect films. The protect films fall into two categories: (1) the relative thick porous diffusion barriers, formed on carbon steels (red rust) and copper alloys (cuprous oxide) and (2) the thin invisible passive films on stainless steels, nickel alloy and other passive metals like titanium. A spectrum of erosion-corrosion process in Table I was summarized by Poulson [3,4]. Actually, this spectrum is more suitable to the metals with loose and less protective surface scale exposed to a single phase flow. The erosion-corrosion mechanisms of passive metals in flowing slurries are much more complicated than those shown in Table I. For example, the mechanical erosion may contribute a major part of total material loss of stainless steels in marine pumping applications

where solid erodent is present, even under the condition that the protect film is only partially removed. A large amount of experimental data have indicated that, even if the corrosion component is very small, e.g. less than 5% of the pure mechanical erosion rate in absence of corrosion, the resulting erosion-corrosion rate may be much greater than that without corrosion [5,6]. With implantation of sand production controls, such as gravel-packing completion, the prone reservoirs produce still sand up to 5 pounds per thousand barrels, which results in considerable material loss due to erosion-corrosion[7]. Experimental evidence indicated that the corrosion due to wet CO₂ might accelerate the erosion of C-Mn steel by a factor of 2-4 [7]. Because of the damage and removal of protective scale caused by the sand impingement, the corrosion rate also increased significantly.

Table I. Spectrum of erosion-corrosion processes [3,4]

Electrochemical dissolution dominated	
Mechanism	Erosion-corrosion rate
Flow thins protective film to equilibrium thickness which is a function of both mass transfer and growth kinetics	The metal loss rate is very low and it is controlled by the dissolution of the protective film
Film is locally removed by dissolution, fluid induced stress or particle/bubble impact and the repassivation occurs simultaneously	The erosion-corrosion rate is a function of film removal, bare metal dissolution rate and subsequent repassivation rate.
Film is removed and does not reform.	It is equal to the dissolution rate of bare metal
Film is removed and underlying metal surface is mechanically damaged, which contributes to the overall metal loss	It is the sum of the dissolution rate of bare metal and the possible synergistic effect of mechanical damage
Film is removed and mechanical damage to the underlying metal is dominant damage mechanism	The direct contribution of corrosion is relatively small.
Mechanical damage dominated	

As mentioned above, two different material loss mechanisms are involved in erosion-corrosion of metals, mechanical erosion and electrochemical corrosion. The mechanical erosion relates to plastic deformation and rupture in surface layer. Small pieces of metal are removed from the surface by various mechanical forces before being ionized. The electrochemical corrosion relates to the metal being dissolved into the slurry after it is ionized. Therefore, the total material loss rate \dot{w} is the sum of material loss rates caused by erosion, \dot{e} , and corrosion, \dot{c} ,

$$\dot{w} = \dot{e} + \dot{c} \tag{1}$$

To be more accurate, the corrosion rate is the more suitable term in the place of “erosion-corrosion rate” in Table I. The total material loss of material in corrosive fluids is normally larger than the sum of those caused by pure mechanical erosion and pure electrochemical corrosion. According to standard of ASTM G119, the pure mechanical erosion is defined as the erosion in an inert environment and the pure electrochemical corrosion is the corrosion under erosion-free condition. The additional wastages of erosion and corrosion components caused by

the synergistic effects are regarded as the corrosion-enhanced erosion, \dot{e}_c , and the erosion-enhanced corrosion, \dot{c}_e ,

$$\dot{e} = \dot{e}_0 + \dot{e}_c \quad (2)$$

$$\dot{c} = \dot{c}_0 + \dot{c}_e \quad (3)$$

The erosion-corrosion mechanism is affected by all the factors which control corrosion and all the factors which affect erosion. In combination, the damage is synergistic and can be extremely aggressive. The synergism of erosion and corrosion, \dot{s} , is expressed as the sum of \dot{e}_c and \dot{c}_e :

$$\dot{s} = \dot{e}_c + \dot{c}_e \quad (4)$$

The synergism often contributes to such a large part of the total material loss, that it cannot be ignored in service lifetime assessment from the engineering perspective. The corrosion in erosive liquid can be determined using the standard procedures used in erosion-free condition, such as the one to measure the linear polarization resistance (ASTM G59) and the one to generate the potentiodynamic curves (ASTM G5). The pure mechanical erosion rate in corrosive slurries should be conducted under the same hydrodynamic conditions under cathodic protection. ASTM G119 recommends polarizing the specimen to one volt cathodic with respect to the open circuit potential to guarantee a fully protected condition. However, caution must be taken because hydrogen embrittlement may occur in some materials under the cathodic protection. Besides, the gas bubbles produced by the hydrogen evolution may affect the hydrodynamic conditions. A recent study indicated that the erosion rates under cathodic protection in the slurries prepared by dilute acidic solutions are much higher than those in neutral and alkaline slurries. In line with ASTM G119, the following dimensionless factors can be defined to describe the degree of synergism:

$$\text{Total synergism factor} = \frac{\dot{w}}{\dot{w} - \dot{s}} = 1 + \frac{\dot{s}}{\dot{e}_0 + \dot{c}_0} \quad (5)$$

$$\text{Corrosion augmentation} = \frac{\dot{c}}{\dot{c}_0} = 1 + \frac{\dot{c}_e}{\dot{c}_0} \quad (6)$$

$$\text{Erosion augmentation} = \frac{\dot{e}}{\dot{e}_0} = 1 + \frac{\dot{e}_c}{\dot{e}_0} \quad (7)$$

Although efforts have been made, it is still difficult to build an integral model of erosion-corrosion. Because a large amount of factors are involved in the erosion-corrosion processes including the metallurgical features of material, the hydrodynamics of fluid and flow field, the characteristics of erodent, the temperature [8] and corrosivity of media.

During impingement, the sand degradation may occur from the breakdown of sand particles and/or the bluntness of particle corner or edge, leading to a reduced erosion rate. If the effect of sand degradation is excluded, the erosion rate under a given hydrodynamic condition is independent of time. The total material loss rate resulted from a cavitating liquid or impingement

of liquid droplets is a function of time. There is an incubation time period within which the rate of material loss is negligible. After the incubation, the material loss rate increases rapidly, reaches a peak value and then reduces to a steady value gradually.

Erosion and Corrosion-Enhanced Erosion

Erosion Resistance and Mechanical Properties of Target Materials

Many mechanical erosion models have been established to correlate the erosion resistance of target materials to their mechanical properties and hydrodynamic parameters. A detailed literature review on this aspect is out of scope of this article. Meng and Ludema [9] provided an exhaustive overview up to 1995, found 182 equations and selected 28 for special study. Lyczkowski and Bouillard [10] did one review up to 2002. As pointed by Tsai et al. [11], over a fairly wide range of variables, at least in flowing slurries, the overall dependence of the particle and target hardness (H_p and H respectively) on erosion is approximately given by $\dot{e}_0 \propto H_p^{1/2} / H$. Generally, the erosion resistance of target materials increases with their hardness if no substantial change takes place in the erosion mechanisms and, as illustrated in Figure. 1, the power law erosion rate of materials can give a fairly good fit to the correlation between the mechanical erosion rate and surface hardness

$$\dot{e}_0 = \kappa_H H^{-n_H} \tag{8}$$

where κ_H and $n_H (> 0)$ are experimental constants depending heavily on the erosion mechanisms.

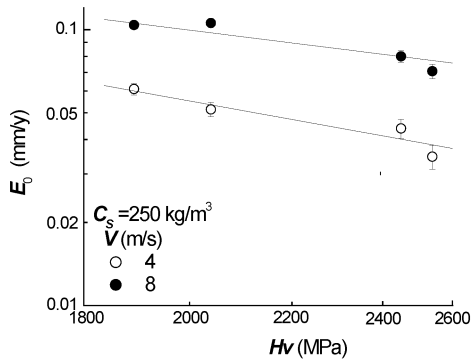


Figure 1. Dependence of erosion rate on the surface hardness.

Corrosion-Induced Degradation of Surface Mechanical Properties

At least two irreversible processes are involved in the erosion-corrosion process, namely, the electrochemical corrosion at surface and plastic deformation in surface layer. The fluxes of these

two irreversible processes can be represented by the corrosion rate \dot{c} (or the anodic current density $i_A = \dot{c}/zF$, where z is the number of electrons involved in the corrosion reaction of the electrode material and F is the Faraday constant) and the plastic strain rate $\dot{\gamma}_p (= \dot{N}\lambda\bar{b}$, where \dot{N} , λ and \bar{b} are the flux, the mean free path and Burger's vectors of dislocations, respectively). When the anodic dissolution on surface and the plastic deformation in surface layer occur simultaneously, they will enhance each other, leading to the synergistic effect [12],

$$\dot{\gamma}_p = \dot{\gamma}_{p,0} + L_{C \rightarrow p} F_C \quad (9)$$

$$i_A = i_{A,0} + L_{p \rightarrow C} F_p \quad (10)$$

where $\dot{\gamma}_p$ is plastic deformation rate in an inert environment, $i_{A,0}$ is the corrosion current density of material free of dynamic plastic deformation, F_C and F_p are the general driving forces for the plastic deformation (such as the force produced by particle impingement) and anodic dissolution (the potential), respectively, $L_{C \rightarrow p}$ and $L_{p \rightarrow C}$ are the coefficients representing the cross effects. The second term in Eq. (10) stands for the mechanical impact enhanced corrosion and it indicates that the anodic dissolution rate increases linearly with the plastic deformation rate [13]. The second term in Eq. (9) implies that the plastic deformation in the surface layer would be promoted by the corrosion occurring on surface. The reduced resistance to the plastic deformation can be characterized by the degradation of surface strength or hardness. The degradation of the surface hardness due to the presence of anodic dissolution, ΔH , can be formulated as follows [9]:

$$\frac{\Delta H}{H} = -B \log \left[\frac{i_A}{i_{th}} \right] \quad (11)$$

where H is surface hardness measured in an inert environment, ΔH is defined as the difference between the hardness values measured in corrosive solution while anodic current is present on surface and in the inert environment. B is a constant related to the active volume of dislocations and test conditions, i_{th} the threshold current to cause the surface strength degradation. The phenomenon of corrosion-induced surface hardness degradation has been experimentally observed in carbon steels and commercial pure iron using the microhardness and nanoindentation techniques. An example of corrosion-induced microhardness degradation is demonstrated in Figure 2.

Corrosion-Enhanced Erosion

If the increasing erosion rate caused by the anodic dissolution-induced hardness degradation is the only mechanism of corrosion-enhanced erosion, the increment of erosion rate $\Delta \dot{e}$ due to the presence of anodic dissolution can be defined as the corrosion-enhanced erosion, namely, $\dot{e}_c = \Delta \dot{e}_0 = \dot{e} - \dot{e}_0$. By combining Eqs. (8) and (11), the normalized corrosion-enhanced erosion wastage, *i.e.*, the wastage ratio of \dot{e}_c / \dot{e}_0 , can be correlated to the anodic current density i_A as follows,

$$\frac{\dot{e}_c}{\dot{e}_0} \approx Z \log\left(\frac{i_A}{i_{th}}\right) \quad (12)$$

where Z is an experimental constant, i_{th} is the threshold anodic current density to cause the corrosion-enhanced erosion. According to Eq. (12), the erosion will be enhanced by the chemo-mechanical effect when corrosion occurs simultaneously, and the erosion augmentation defined by ASTM G119 ($=1 + \dot{e}_c / \dot{e}_0$) will be approximately a linear function of the logarithm of anodic current density. It has been shown that the prediction of Eq. (12) agrees well with the experimental results obtained from carbon steels, as shown in Figure 3. In engineering practice, the slurry pipe is normally operated under open circuit potential (OCP). The experiments in Ref. [12] indicated that the corrosion-enhanced erosion at the OCP was predictable using the curve obtained under galvanostatic control as the corrosion current density at the OCP is known.

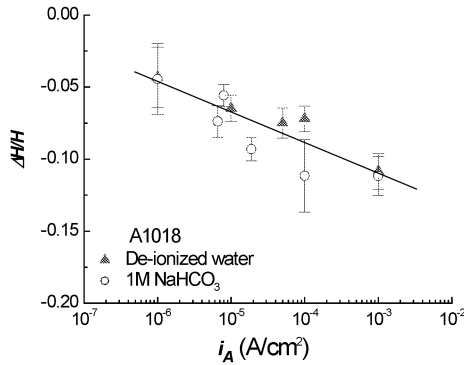


Figure 2. Relationship between the normalized hardness drop and anodic current density.

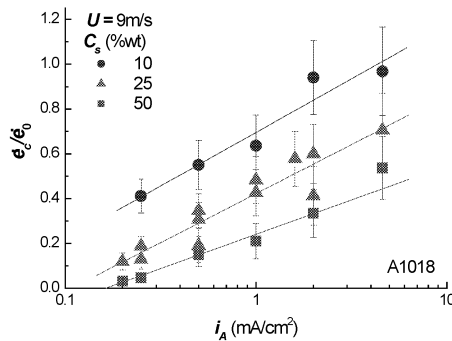


Figure 3. Effect of anodic current density on normalized corrosion-enhanced erosion rate.

As shown in Figure 3, the corrosion-enhanced erosion is also affected by the concentration of solid particles in slurry when the anodic current density is held unchanged. The impact the sand concentration can be predicted when the normalized wastage ratio, \dot{c}/\dot{e}_0 , is employed to replace anodic current density, as shown in Figure 4. Our experimental results demonstrate that the corrosion-induced erosion is also observable in flowing electrolyte free of solid particles.

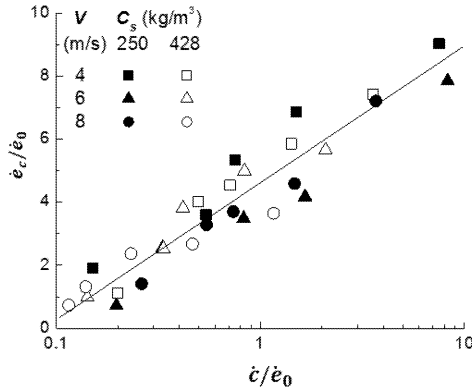


Figure 4. Correlation between normalized mechanical erosion rate and wastage ratio \dot{c}/\dot{e}_0 under galvanostatic control [12].

Until now, it is still difficult to build a universal model for the corrosion-enhanced erosion because of mechanisms complexity. A recent research [14] indicated that when the hydrodynamic condition and anodic current density were held unchanged, the erosion rates of carbon steel in acidic slurries were significantly higher than those in alkaline or near-neutral slurries. The erosion rates in corroding slurries with high or near-neutral pH were not affected by the slurry chemistry but the slurry chemistry impact was pronounced in acidic slurries. The high-to-low order of erosion rates was the same as that of *in-situ* nanoindentation hardness measured in the same corroding environments, indicating that the anodic dissolution-induced surface hardness degradation is likely the mechanism for the high erosion wastage in acidic slurries.

In order to mitigate erosion-corrosion, a careful design of flow geometry can effectively to minimize erosion-corrosion caused by disturbed flow, such as limiting weld root protrusion and steps of flanges, utilizing long radius elbows and gradual changes in the flow cross-section, and replacing the elbow with plugged tee. In the two-phase liquid/solid flow, the erosion-corrosion performance relies on both the mechanical properties and electrochemical characteristics. Generally, an increase of Cr-content in steels will improve the erosion-corrosion resistance. Other good methods include application of coating, surface hardening techniques, application of inhibitor and chemical control.

Summary

A series of models to assess the synergistic effect in slurry erosion process are reviewed. Experimental investigations indicated that the normalized surface hardness dropped as the anodic current density increased. As the results of corrosion-induced surface softening, the erosion rate increased as the corrosion became more severe. The quantitative relationships, (1) between the degradation of the surface hardness and corrosion rate, (2) between the normalized corrosion-enhanced erosion rate and the anodic current density, were established. Some methods to mitigate erosion-corrosion were proposed, such as: proper design, surface treatment, material selection and chemical control.

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References

1. B.T. Lu, and J.L. Luo, "Synergism of electrochemical and mechanical factors in erosion-corrosion," *Journal of Physical Chemistry B.*, 110 (2006), 4217-4231.
2. R.J.K. Wood, "Erosion-corrosion interactions and their effect on marine and offshore materials," *Wear*, 261 (2006), 1012-1023.
3. B. Poulson, "Electrochemical Measurements in Flowing Solutions," *Corrosion Science*, 23 (1983), 391-430.
4. B. Poulson, "Complexities in predicting erosion corrosion," *Wear*, 233 (1999), 497-504.
5. P. Andrews, T.F. Illson, and S.J. Matthews, "Erosion-corrosion studies on 13 Cr steel in gas well environments by liquid jet impingement," *Wear*, 233 (1999), 568-574.
6. C.H. Pitt, and Y.M. Chang, "Jet Slurry Corrosive Wear of High-Chromium Cast-Iron and High-Carbon Steel Grinding Ball Alloys," *Corrosion*, 42 (1986), 312-317.
7. R. Hamzah, D.J. Stephenson, and J.E. Strutt, "Erosion of Material Used in Petroleum Production," *Wear*, 186 (1995), 493-496.
8. B.T. Lu, J.L. Luo, F. Mohammadi, K. Wang, and X.M. Wan, "Correlation between repassivation kinetics and corrosion rate over a passive surface in flowing slurry," *Electrochimica Acta*, 53 (2008), 7022-7031.
9. H.C. Meng, and K.C. Ludema, "Wear Models and Predictive Equations - Their Form and Content," *Wear*, 181 (1995), 443-457.
10. R.W. Lyczkowski, and J.X. Bouillard, "State-of-the-art review of erosion modeling in fluid/solids systems," *Progress in Energy and Combustion Science*, 28 (2002), 543-602.
11. W. Tsai, J.A.C. Humphrey, I. Cornet, and A.V. Levy, "Experimental-Measurement of Accelerated Erosion in a Slurry Pot Tester," *Wear*. 68 (1981), 289-303.
12. B.T. Lu, J.L. Luo, H.X. Guo, and L.C. Mao, "Erosion-enhanced corrosion of carbon steel at passive state," *Corrosion Science*, 53 (2011), 432-440.
13. R.G. Raicheff, Damjanov.A, and J.O.M. Bockris, "Dependence of Velocity of Anodic Dissolution of Iron on Its Yield Rate under Tension," *Journal of Chemical Physics*, 47 (1967), 2198-2199.
14. K. Wang, B.T. Lu, and J.L. Luo, "Investigation of corrosion enhanced erosion of carbon steel in slurries using nanoindentation," *Canadian Metallurgical Quarterly*, 50 (2011), 181-185.