

Corrosion Mechanisms in Near-Neutral pH Stress Corrosion Cracking

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Contributor: Shamsuddeen Ashurah Abubakar, Stefano Mori, Joy Sumner

The two major corrosion mechanisms encountered during stress corrosion of carbon steels in a near-neutral pH environment are anodic dissolution and hydrogen embrittlement. Anodic dissolution, also known as metal dissolution, is a process in which the metal is dissolved from the anodic site during corrosion process, and gases are released from the cathodic site and at the metal surface. This in turn reduces the wall strength and may lead to premature pipeline failure. Hydrogen embrittlement can be defined as the reduction of a metal's tensile strength and ductility due to diffusion of hydrogen atoms into the metal's crystalline lattices during a corrosion process. It causes premature brittle fracture of normally ductile metals under applied stress usually less than the yield strength of the metal.

Keywords: stress corrosion cracking ; pipeline steels ; applied stress

1. Introduction

Pipelines are intended to transport various types of fluids (liquid or gas), mixtures of fluids, solids, fluid–solid mixtures, or capsules (freight-laden vessels or vehicles moved by fluids through a pipe) ^[1]. They are considered to be a safe, effective and economic means of oil and gas transportation across the globe and have a good safety record ^{[2][3]}. However, they can suffer from corrosion.

Corrosion is defined as the destruction or deterioration of a metal that results from a reaction with its environment ^{[4][5][6]}. Corrosion in both offshore and onshore pipelines is a natural occurring phenomenon and is regarded as one of the major causes of pipeline failures ^{[2][4]}, with corrosion damage accounting for about 20–40% of recorded pipeline failures and incidents ^[7]. In 2013, the National Association of Corrosion Engineers (NACE) estimated that the global cost of corrosion was USD 2.5 trillion, which is equivalent to 3.4% of the global gross domestic product (GDP) ^[8].

When pipelines are under stress, for example, from internal fluid movement or other outside forces, and are in the presence of a corrosive environment, they can be susceptible to stress corrosion, commonly known as stress corrosion cracking (SCC). Stress corrosion cracking is caused by the combined action of simultaneous mechanical stress and a specific corrosive media that a metal or alloy is susceptible to ^{[9][10]}. For SCC to occur on a metal or alloy surface, the following three conditions must be met simultaneously: specific conditions to promote crack-propagation must be present; the metallurgy of the material must be susceptible to SCC; and there must be an applied tensile or static stress that exceeds a threshold value ^{[10][11][12]}. This tensile stress can originate from centrifugal forces, external loads, temperature variations or internal stresses induced by heat treatment. Stress may also result from locked-in residual stress from fabrication or welding ^{[9][11]}. SCC cracks normally propagate trans-granularly and/or inter-granularly or may be branched depending on the type of metal/corrosive media combination ^{[9][10][11][12]}. In the trans-granular mode of cracking, the crack advances without a defined preference for the grain boundaries, while in the intergranular mode, the crack proceeds along the grain boundaries.

Generally, two types of SCC have been outlined for pipeline carbon steels in the literature: high pH SCC and near-neutral pH SCC ^{[13][14][15][16][17]}. High pH SCC is characterised by an intergranular mode of cracking and has been investigated in concentrated carbonate/bicarbonate environments with pH values higher than 9 ^{[13][14][15][16][17]}. Conversely, near-neutral SCC (pH = 6–8) is characterised by a trans-granular cracking mode and is associated with dilute carbonate/bicarbonate medium ^{[13][14][15][16][17]}.

The susceptibility of a metal to SCC is affected by several factors; namely: the chemical composition and microstructure of the alloy; the temperature of the environment; the presence of oxidizers in the corrosive medium (O₂, CO₂, H₂S, etc.); the composition and concentration of the corrosive medium; the stress; and the pH of the medium ^{[6][12][18]}.

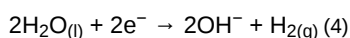
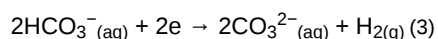
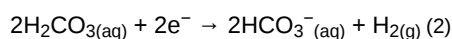
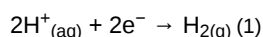
These factors are explored in more detail in the following sections with a brief introduction below. In terms of temperature dependence, SCC is accelerated by increasing temperatures as in most chemical reactions. However, the type of corrosive environment also determines the cracking behaviour of metals or alloys at a particular temperature [6][12]. The presence of oxidizers such as dissolved oxygen, carbon-dioxide or other oxidizing species (including ferric ions in corrosive environments) have a pronounced influence on the cracking susceptibility of metals or alloys [6][19][20]. These oxidizers, when present in high amounts, increase the aggressiveness of corrosive medium, by accelerating the oxidation reaction of the metals, leading to high anodic dissolution and subsequent failure [12][13][18]. Johnson et al. [21] stated that increasing CO₂ concentration from 0.5% to 25% in NS4 solution (near-neutral simulated soil) accelerates crack growth rate during cyclic loading.

Pipeline steels are made up of several types of microstructures; namely austenite, pearlite, ferrite, bainite, martensite, etc. Ferrite grains can further be classified into acicular ferrite, polygonal ferrite, allotriomorphic ferrite, globular ferrite and idiomorphic ferrite [22]. Microstructures that are more susceptible to SCC are characterised by high yield strength, high residual stress, high hardness, small and fine grain shapes and relatively low or entirely absent grain boundaries precipitates [6][23]. Low grain boundary precipitates result from low mill annealing temperature ($T < 1000\text{ }^{\circ}\text{C}$). Mill annealing temperature also determines the grain size of a metal or alloy. Grain size decreases with decreasing mill annealing temperature [22].

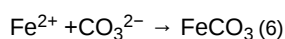
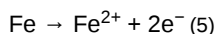
2. Corrosion Mechanisms in a Near-Neutral pH SCC

The major corrosion mechanisms observed during SCC of pipeline carbon steels in a near-neutral solution are anodic dissolution and hydrogen embrittlement. Papavinasam [12], Sastri [11] and Cicek [9] defined hydrogen embrittlement as the loss or reduction of a metal's tensile strength and ductility due to diffusion of hydrogen atoms into the metal's crystalline structures during a corrosion process.

Hydrogen atoms are primarily produced from electrochemical processes such as aqueous corrosion, acid pickling or electroplating. They can also be produced during the cathodic reduction reaction taking place during the corrosion process of metals in acidic solutions, such as hydrogen sulphide (H₂S) or hydrogen fluoride (HF) [10][12]. Hydrogen embrittlement causes premature brittle fracture of normally ductile metals under applied stresses less than the yield strength of the metal [10]. Hydrogen embrittlement of carbon steels commonly encountered in an aqueous medium involves CO₂. The corrosion reactions can be explained thus: CO₂ combines with H₂O to form H₂CO₃ (carbonic acid), H₂CO₃ then further dissociates into HCO₃⁻, H⁺ and CO₃²⁻ [24][25]. The major cathodic reactions are the reduction of H⁺, H₂CO₃ and HCO₃⁻ as expressed below [26][27]:



According to Nesic et al. [26] and Mu and Zhao [27], the reduction of H₂CO₃ and HCO₃⁻ is the dominant reaction at pH values of 4–6 in aqueous CO₂ medium, whereas the H⁺ reduction reaction is more significant at lower pH values. The major anodic reactions are the dissolution of Fe (iron) followed by FeCO₃ (iron carbonate) formation as shown below [26][27]:



Anodic dissolution, also known as metal dissolution, is a process in which the metal is dissolved from the anodic site during corrosion processes, and gases are released from the cathodic site and at the metal surface [28]. The rate of metal dissolution in an electrochemical reaction is higher when it is in an active state in comparison to the passive state. It also depends on the corrosive medium's composition and environmental conditions [6].

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