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油气开采环境下管道的协同腐蚀及 防护研究进展^{*}

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摘要: 服役于高温高压 CO₂ / H₂S 环境下的管道腐蚀是油气田中急需解决的重要问题。CO₂、H₂S 及 Cl⁻ 是油气田管道中常见的腐蚀介质, 其与温度、压力、pH值、含水率、流速等外界因素间的协同腐蚀作用会导致管道严重腐蚀, 研究这些腐蚀介质与外界因素的协同腐蚀机制以及减缓管道腐蚀的措施有着重要的科学意义和经济价值。针对油气开采过程中金属管道的腐蚀问题, 综述了 CO₂、H₂S 及 Cl⁻ 在协同腐蚀过程中起到的作用, 讨论了温度、压力、pH 值、含水率及流速等实际工况条件下外界因素对腐蚀过程的影响。论述了现有管道腐蚀防护技术与工艺的特点: 合金元素的掺杂可以改善腐蚀形貌, 提高腐蚀产物层的致密性, 等离子体扩渗与镀膜技术能够制备一层致密的保护层来吸收部分腐蚀介质并减缓腐蚀速率, 缓蚀剂的添加可以减缓管道的阴极或阳极反应或形成减缓腐蚀速率的吸附层。最后展望了未来油气田管道防护技术的发展方向: 为了有效地对油气开采环境下的管道进行保护, 需要进一步研究腐蚀介质和外界因素间的协同腐蚀作用, 模拟实际工况下的腐蚀环境, 对等离子体扩渗与镀膜技术、缓蚀剂等现有的防护技术进行系统的试验测试。

关键词: 油气管道; CO₂ / H₂S 腐蚀; 影响因素; 表面防护; 等离子体

中图分类号: TE832

Research Progress in Synergetic Corrosion and Protection of Pipelines in Oil and Gas Production Environment

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Abstract: Pipeline corrosion in CO₂ / H₂S environments at high temperatures and pressures is a critical problem in oil and gas fields that must be solved urgently. CO₂, H₂S, and Cl⁻ are common corrosion media in oil and gas pipelines. CO₂ changes the chemical properties of water in a solution and decreases the pH value of the solution, which promotes cathodic hydrogen evolution reaction. Corrosive ions dissociated from H₂S exhibit strong penetrability, which accelerates pitting and sulfide stress cracking. The barrier function and catalytic effects of Cl⁻ reduce the adhesion of corrosion products, which accelerates metal corrosion. The synergistic corrosion between CO₂, H₂S, Cl⁻, and external factors, such as temperature, pressure, pH value, water content, and flow rate, leads to

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the severe corrosion of pipelines. These external factors impact the corrosion process by influencing the morphology of the corrosion products. A harsh corrosion environment loosens the corrosion products and weakens the barrier effect of the corrosion products on the corrosive medium, thereby accelerating the corrosion of the substrate. Thus, it is necessary to investigate the synergistic corrosion mechanisms of corrosive media and external factors and to propose measures to mitigate pipeline corrosion. In view of the corrosion problem of metal pipelines encountered during oil and gas exploitation, the roles of CO_2 , H_2S , and Cl^- in the synergistic corrosion process are summarized in this paper. In addition, the effects of external factors, such as temperature, pressure, pH value, water content, and flow rate, on the morphology and composition of corrosion products under actual working conditions are discussed. The characteristics of existing pipeline corrosion protection technology and processes are discussed. Doping with alloy elements can modify the composition of the corrosion products and improve the corrosion morphology and compactness of the corrosion product layer. Doping with elements, such as Ni, Cr, Mo, and Ti, can effectively slow the pitting and stress corrosion cracking of metals. Plasma diffusion and coating technology can be applied to prepare a dense protective layer to absorb a part of the corrosion medium and decrease the corrosion rate. The corrosion resistance of a metal is effectively improved by infiltrating interstitial atoms into the metal surface using chemical heat treatment techniques, such as nitriding, carburizing, and carbonitriding. The addition of a corrosion inhibitor can slow the cathodic or anodic reaction of the pipeline, or form an adsorption layer to decrease the corrosion rate. However, traditional measures for protecting oil and gas pipelines, such as the use of corrosion-resistant alloys and corrosion inhibitors, are limited owing to their high operating costs and environmental pollution. The preparation of advanced coatings on the inner surfaces of pipelines is expected to achieve a compromise between corrosion protection and cost, and is one of the most effective methods for protecting metal pipelines. Ni-P coatings effectively decreases the corrosion rate by absorbing the corrosive medium to generate corrosion products. Diamond-like carbon films prepared via hollow cathode plasma-enhanced chemical vapor deposition on the inner surfaces of pipelines are also considered one of the most effective methods for future oil and gas field pipeline protection because of their excellent chemical inertness and minimal chemical reactions with acids, alkalis, and salts. Finally, future directions for the advancement of pipeline protection technology in oil and gas fields are proposed. It is necessary to further investigate the synergistic corrosion effect between corrosive media and external factors, and simulate the corrosion environment under actual conditions to effectively protect pipelines in oil and gas production environments. This can be achieved by conducting systematic experimental tests on existing protection technologies, such as plasma diffusion and coating technology, and using corrosion inhibitors.

Keywords: oil and gas pipelines; $\text{CO}_2 / \text{H}_2\text{S}$ corrosion; influence factors; surface protection; plasma

0 前言

随着全球经济的发展,石油、天然气能源的需求持续增加,为了提高油气开采效率, CO_2 驱技术被广泛应用在油气田中^[1]。然而,对于含硫油气田, CO_2 驱技术会导致油气管道长期处于 $\text{CO}_2 / \text{H}_2\text{S}$ 环境,再加上地层水中含有较高的 Cl^- , CO_2 、 H_2S 和 Cl^- 等腐蚀介质间的协同作用,会导致油气管道加速腐蚀^[2-3]。同时,由于油气田环境复杂,高温、高压等外界因素能够协同腐蚀介质加速腐蚀过程^[4],引发管道的穿孔、失效等,使油气泄露甚至引发安全事故^[5]。为了有效还原油气开采过程中的管道腐蚀行为,研究者采用模拟油气田现场工况环境的方式研究了温度、压力、流速、含水率及pH值等不同腐蚀因素下管道的腐蚀行为与腐蚀机理^[6-8]。

油气开采过程中的管道腐蚀是一个不可避免的

问题,但通过适当的处理可以减缓腐蚀的速率,延长管道的使用寿命。腐蚀过程中的腐蚀产物形貌是影响管道耐蚀性的一个重要因素^[9],合金元素的掺杂可以使管道合金化来改变腐蚀形貌,提高腐蚀产物层的致密性,从而使管道耐蚀性能提高^[10]。另外,与腐蚀产物层作用相似的涂层材料也是提高管道耐蚀性的一个有效方法,等离子体镀膜技术制备的致密涂层能够阻隔腐蚀介质与管内壁的直接接触,同时涂层厚度的提高能延长腐蚀介质的渗透路径,起到减缓腐蚀速率的作用,两方面共同提高管道耐蚀性^[11]。此外,等离子体扩渗技术与缓蚀剂的使用也可以有效减缓管道的腐蚀。管道的合金化(Ni、Gr、Mo元素)、涂层材料(DLC涂层、Ni-P涂层)及新型环保缓蚀剂逐渐成为腐蚀研究的热门领域。

本文综述了油气开采环境下管道的协同腐蚀与防护方法,分别阐述了 CO_2 、 H_2S 、 Cl^- 及外界因素在腐蚀中起到的作用,并从金属的表面处理、金属

的合金化与缓蚀剂三个方面阐述了现有腐蚀防护技术特点与防护效果,为我国油气管道腐蚀与防护技术发展提供支撑。

1 CO₂/H₂S与环境因素的协同腐蚀

1.1 CO₂在腐蚀中的作用

CO₂可以通过改变溶液的水化学特性来影响管道的腐蚀,引入CO₂后,溶液的H⁺浓度上升,阴极析氢反应的速率得到增强^[12],腐蚀机理如图1所示,CO₂溶解在水中的反应如下^[13-14]:

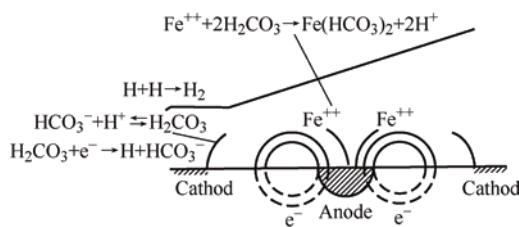
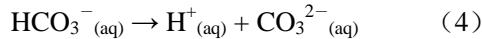
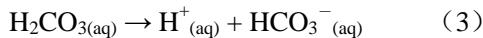
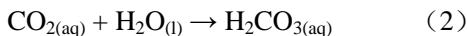
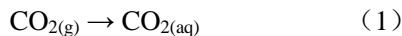


图1 CO₂腐蚀机理图^[14]

Fig. 1 CO₂ corrosion mechanism^[14]

溶液水化学特性的改变会影响腐蚀产物的成分与致密性,增强氢的渗透,加速金属的腐蚀^[15-16]。随着溶液中CO₂分压的增加,CO₂腐蚀产物的晶粒尺寸变粗,疏松的腐蚀产物层无法对基底起到足够的保护效果,腐蚀介质能够轻易渗透到基底造成金属的进一步腐蚀^[17]。当处于临界温度(31.1 °C)与临界压力(7.38 MPa)时,CO₂会转变为超临界流体状态,由于此时CO₂的溶解度远大于低压条件,管道的电化学腐蚀速率会大幅提高^[18],因此,超临界CO₂条件下管道的腐蚀行为研究逐渐成为CO₂腐蚀领域的热点问题。

1.2 H₂S在腐蚀中的作用

在H₂S环境中管道的两种典型失效形式是氢致开裂(HIC)和硫化物应力开裂(SSC)^[19],H₂S溶于水会电离出氢离子,氢扩散到金属表面后会渗透到金属内部并在缺陷部位发生氢脆,大幅缩短管道的使用寿命。管道被腐蚀产生的腐蚀产物层能降低腐蚀介质的渗透速率,从而减缓钢的进一步腐蚀^[20]。但是H₂S解离出的腐蚀性离子H⁺、HS⁻及S²⁻能穿透腐蚀产物层向基底渗透,导致管道持续腐蚀,并且LEI等^[21]的研究表明,腐蚀产物层的生长会因为基

底与阻挡膜界面氢泡的聚集而被抑制,导致管道后续的耐蚀性降低。图2为氢对金属钝化行为的影响示意图,H₂S水解平衡反应如下:

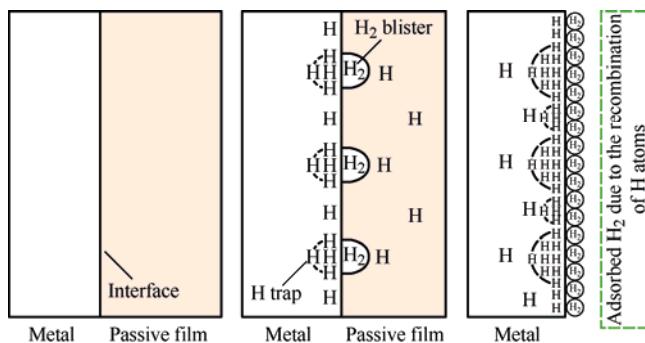
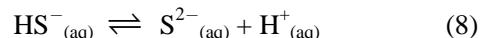
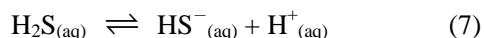
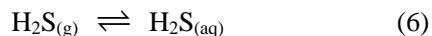
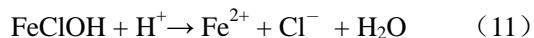
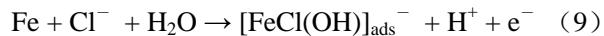


图2 氢对金属钝化行为的影响示意图^[21]

Fig. 2 Influence mechanism of hydrogen on metal passivation behavior^[21]

1.3 Cl⁻在腐蚀中的作用

Cl⁻大量存在于油气开采的地层水中,它的存在会局部击穿钝化膜并加剧金属的点蚀^[22],在油气环境中对管道的腐蚀起着重要的促进作用。Cl⁻的离子半径小,穿透能力强,使其可以穿过腐蚀产物层并吸附在基底表面,降低腐蚀层与基底间的粘附力^[23],富集的Cl⁻在腐蚀过程中会起到催化的作用^[24],从而加速阳极的溶解。Cl⁻浓度的提高会增加腐蚀速率^[7,25],同时硫化物与氯化物间具有协同腐蚀作用,在腐蚀过程中硫化物被整合到钝化膜中,从而使基底表面形成不均匀凹坑,有助于氯化物的进一步渗透^[26]。在90 °C的H₂S-NaCl溶液中,Cl⁻成为金属失效的主要因素,应力腐蚀开裂的机制从由氢诱导的开裂,转变为由氯诱导的阳极溶解引发的开裂^[27]。图3为Cl⁻在腐蚀中的作用机理示意图,Cl⁻的催化作用方程式如下:



1.4 油气田环境中影响腐蚀的因素

油气开采环境下的管道长期处于一个复杂多变的环境,高温、高压、动态流动等环境协同CO₂/H₂S导致了管道的严重腐蚀,这些环境因素一方面可以影响阳极铁的溶解和阴极的析氢反应速率^[28],另一方面可

以使腐蚀产物层的成分与厚度改变, 进而影响腐蚀产物对氢渗透的阻挡能力^[29], 两者结合共同影响管道的腐蚀速率。腐蚀产物的组成与形貌是影响腐蚀行为的一个重要组成部分, 因此, 后续的讨论将在腐蚀机理的基础上考虑各种环境因素对腐蚀产物的影响。

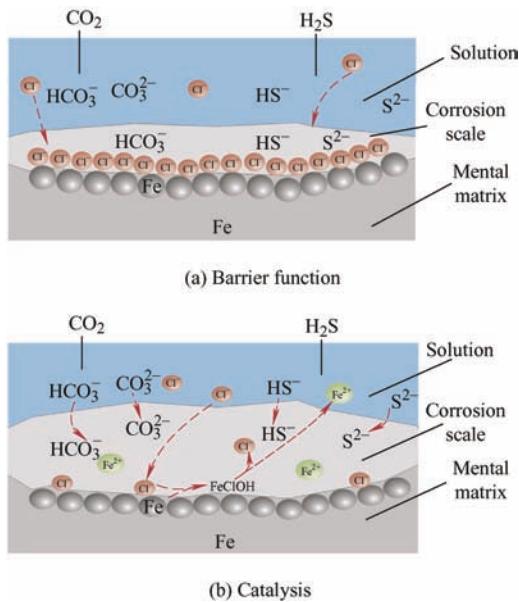


图 3 Cl^- 在腐蚀中的作用机理示意图^[23]

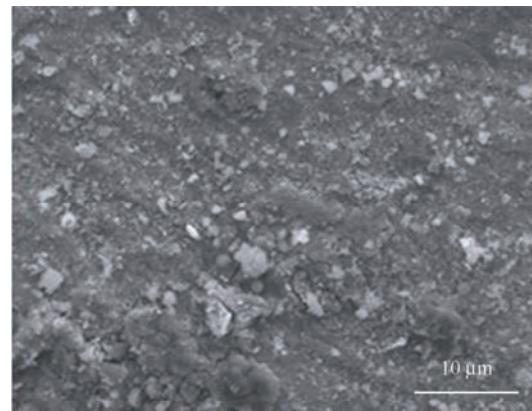
Fig. 3 Schematic diagram of the mechanism of Cl^- in corrosion^[23]

1.4.1 温度、压力与 pH 值

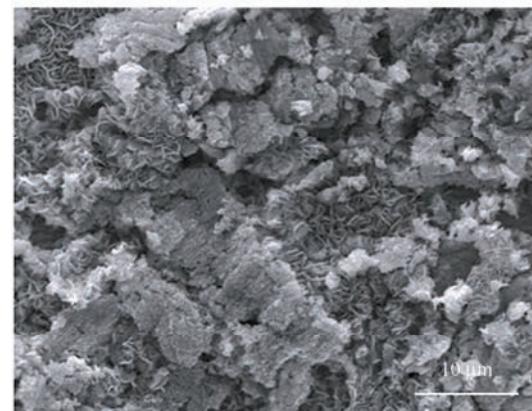
温度对腐蚀速率的影响受到界面的反应速率与腐蚀产物生成速率的共同作用, 温度升高会使 H^+ 的溶解度升高, 导致界面的反应更加剧烈, 但界面反应速率的增加, 会加快腐蚀产物的生成速率, 腐蚀产物层的生成可以有效的降低腐蚀速率^[30], 当温度超过某一值后, 腐蚀速率出现拐点开始下降。但是近期有研究发现, 高温虽然有利于腐蚀产物的积累, 但也会增加腐蚀产物的缺陷, 随着温度从 30 °C 上升到 130 °C, 316 不锈钢的耐蚀性急剧下降^[9]。因此, 研究者在研究温度与管道腐蚀时, 应同时考虑腐蚀产物生成速率与腐蚀产物的致密性。

国内外学者普遍认为, CO_2 与 H_2S 共存体系下的腐蚀行为与二者分压有关^[7, 31-32], 当 CO_2 分压较高, 腐蚀过程由 CO_2 主导时, 生成致密的腐蚀产物 FeCO_3 使管道的耐蚀性提高。而当腐蚀过程由 H_2S 主导时, CO_2 腐蚀中典型的腐蚀产物 FeCO_3 的生成会因为 $\text{FeHS}_{\text{ads}}^+$ 的优先吸附机制而被抑制^[33], 腐蚀产物层变得松散甚至脱落, 管道的耐蚀性降低, 溶解的 CO_2 等腐蚀物质能够轻易地到达钢表面, 加速钢基底的溶解, 使腐蚀速率提高^[34]。 H_2S 能增加腐蚀产物层的缺陷, 因此, 在腐蚀过程中 H_2S 浓度的增加会加剧管道的局部腐蚀^[6]。

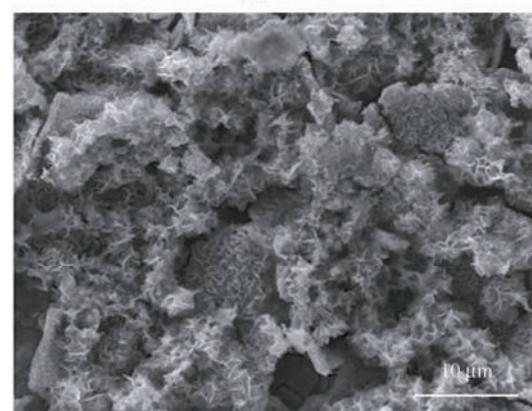
与中性溶液相比, 酸性溶液中的 H^+ 浓度更高, 管道表面阴极的析氢反应更加剧烈, 同时 pH 值降低会增加腐蚀产物的溶解度, 导致管道钢的耐蚀性也随之恶化, 最终使腐蚀速率提高, 管道钢在不同 pH 值 H_2S 溶液中的腐蚀形貌如图 4 所示, 随溶液 pH 值的降低, 腐蚀产物层的致密性明显降低^[29]。此外, 在存在 Cl^- 的环境中, 随着溶液 pH 值的降低, 点蚀的电位变得更负, 钝化范围变得更窄, 较低的 pH 值会加剧点蚀的敏感性, 使腐蚀更加严重^[27]。



(a) pH5.5



(b) pH4.5



(c) pH3.5

图 4 不同 pH 值的 H_2S 溶液中的腐蚀形貌^[29]

Fig. 4 Corrosion morphology in H_2S solution with different pH values^[29]

1.4.2 含水率与流速

油气田中的含水率是影响管道腐蚀的一个重要因素，在实际油气田环境中，管道面临的是原油-水气的多相环境，水与管道的接触面积因为原油的润湿而被减少，并且由于原油的吸附，管道表面水相的电化学特性改变，从而影响了腐蚀产物膜的形态、组成和结构^[35]。管道处于含水率0%的纯原油环境中时几乎不会发生腐蚀^[36]，只有当原油中存在能溶解腐蚀性物质的水，并且水能直接接触到管道时，腐蚀才会发生^[37]。因此，含水率在腐蚀过程中起着重要的作用，是一个需要细致研究的影响因素。

油水混合物分为低含水率(水相体积小于26%)的油包水乳液、高含水率(水相体积大于74%)的水包油乳液以及中等含水率的水油共存状态。当处于低含水率时，管道内表面会被油相吸附润湿，腐蚀性的水相很难与管道接触，只发生较低程度的腐蚀。中等含水率时，管道内油水混合物转变为水包油与油包水乳液共存的状态，被油相覆盖的部分腐蚀较慢，而被水相浸润的部分发生剧烈腐蚀，所以总体呈现出局部腐蚀的状态。当处于高含水率时，管道被水相大部分的润湿，腐蚀明显加剧。总体来说，油气田环境下，随着含水率的升高，管道的腐蚀速率升高，从中等含水率进入高含水率后，腐蚀速率的升高明显加快^[38]，如图5所示。因此，当油气的开采进入高含水量阶段时，需要考虑采取必要的措施来对管道进行保护。

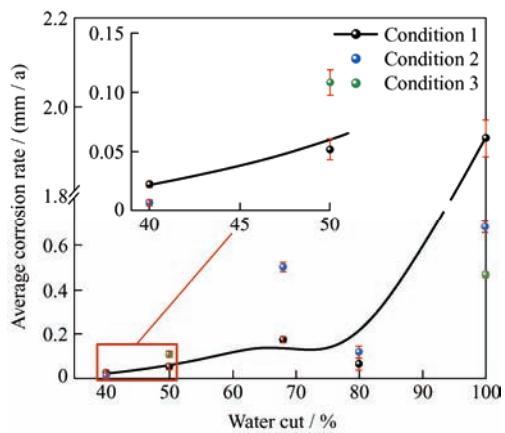


图5 85 °C的CO₂-H₂S环境下含水率对平均腐蚀速率的影响^[38]

Fig. 5 Effect of water content on average corrosion rate in CO₂-H₂S environment at 85 °C^[38]

由于腐蚀环境的差异，向油气田中注入CO₂后管道可能会处于两种恶劣的腐蚀环境，一种是饱和蒸气CO₂/H₂S，另一种是向含水层注入CO₂后得到的饱和盐水CO₂/H₂S，这两种腐蚀环境下的管道具有不同的腐蚀形貌以及腐蚀速率，同时腐蚀产物形

成的过程也存在差异。饱和蒸气环境下腐蚀是从蒸气在试样表面冷凝时开始的，冷凝过程产生的冷凝液滴随机分布，并未完全覆盖试样表面，而在饱和盐水环境中，由于存在能溶解腐蚀性物质的水，腐蚀性离子均匀分布。因此，饱和盐水CO₂/H₂S环境下的腐蚀速率更高，形成的晶体尺寸更大。在腐蚀过程中，含水率的差异造成电解质分布的差异，饱和蒸气下的腐蚀产物形成于随机分布的液滴中，而饱和盐水环境下的腐蚀产物均匀析出，最终导致了腐蚀速率的差异，蒸气饱和H₂S/CO₂环境和H₂S/CO₂饱和盐水环境中形成的腐蚀产物示意图如图6所示。

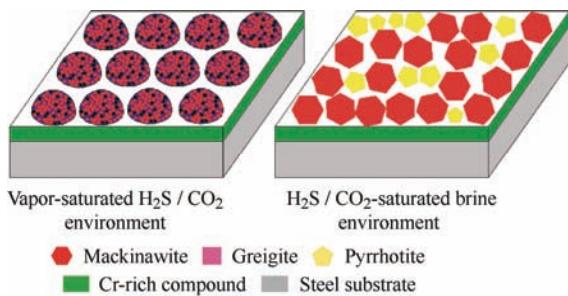
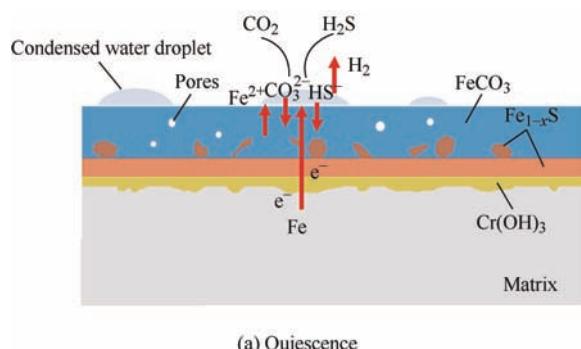


图6 蒸气饱和H₂S/CO₂环境和H₂S/CO₂饱和盐水环境中形成的腐蚀产物的示意图^[39]

Fig. 6 Schematic representation of corrosion products formed in a steam-saturated H₂S/CO₂ environment and a H₂S/CO₂ saturated brine environment^[39]

原油能够吸附在管道内表面来减缓腐蚀速率，但吸附油相的屏蔽作用不足以抵抗流体流动的冲刷作用，在流体的冲刷下，水相能够与管道表面接触并发生CO₂/H₂S腐蚀，因此流体的流速也会影响管道的腐蚀。高流速能增加管道表面的传质速率，提高均匀腐蚀的速率，但腐蚀速率的加快影响腐蚀产物的生成速率，腐蚀产物层得到更快的积累，使得整体的腐蚀速率降低。但同时，高流速会破坏局部的腐蚀产物，增加了点蚀的速率^[40]，动态超临界CO₂与H₂S共存环境中的腐蚀示意图如图7所示，在流动腐蚀条件下，先是腐蚀产物FeCO₃的生成被抑制，管道耐蚀性降低，其次会使管道的凹坑中聚集更多腐蚀介质，加速点蚀的发生^[41]。



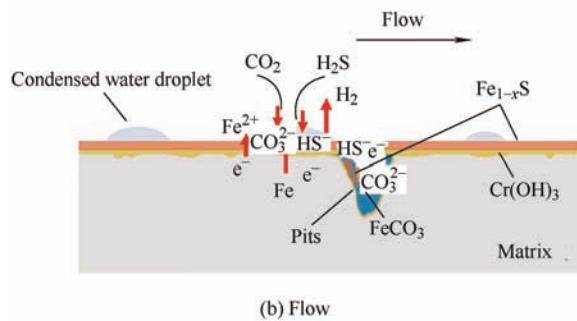
图 7 动态超临界 CO_2 与 H_2S 共存环境中的腐蚀示意图^[41]

Fig. 7 Corrosion mechanism in dynamic supercritical CO_2 and H_2S coexistence environment^[41]

2 减缓管道在油气田环境下腐蚀的方法

2.1 等离子体扩渗技术

通过等离子体渗碳、渗氮或碳氮共渗等化学热处理技术将间隙原子渗入金属表面可以提高金属在 $\text{CO}_2 / \text{H}_2\text{S}$ 环境中的耐蚀性, 降低腐蚀速率。LI 等^[42]

通过低温液体氮化技术使 304 奥氏体不锈钢表面产生由顶部氧化物层、中部富氮层和底部富碳层组成的三层结构, 如图 8a 所示。氧化层和氮化层降低了氢的扩散系数, 减少了原子进入材料的数量, 提高了材料的抗氢脆能力。同时, 氮化层减少了腐蚀产物的产生, 活性的氮原子可以与 H^+ 结合以避免 pH 值的降低, 从而减缓 H_2S 的腐蚀速率^[42]。在 H_2S 溶液中浸泡 720 h 后的样品横截面如图 8 所示, 未处理的样品横截面上能观察到许多凹坑和裂纹, 表面形成大量的腐蚀产物, 而在氮化样品的横截面上没有发现凹坑和裂纹, 表面仅产生很少的腐蚀产物, 表明渗氮处理可以有效提高 304 不锈钢在 H_2S 环境中的耐蚀性。后续为了改善不锈钢在含氯溶液中的裂缝与点蚀, 通过低温液氧氮化引入了厚度为 26 μm 的 S 相层^[43], 低温下的氮化处理提高了点蚀电位, 改善了缝隙的腐蚀性能, 并且 Fe_3O_4 层有效地阻挡了腐蚀性离子, 使腐蚀介质难以穿透钢材。等离子体渗碳、渗氮技术能使不锈钢具有极高的硬度及抗疲劳性, 阻挡层的存在极大提高了其原有的耐蚀性, 是一种优秀的表面处理技术。

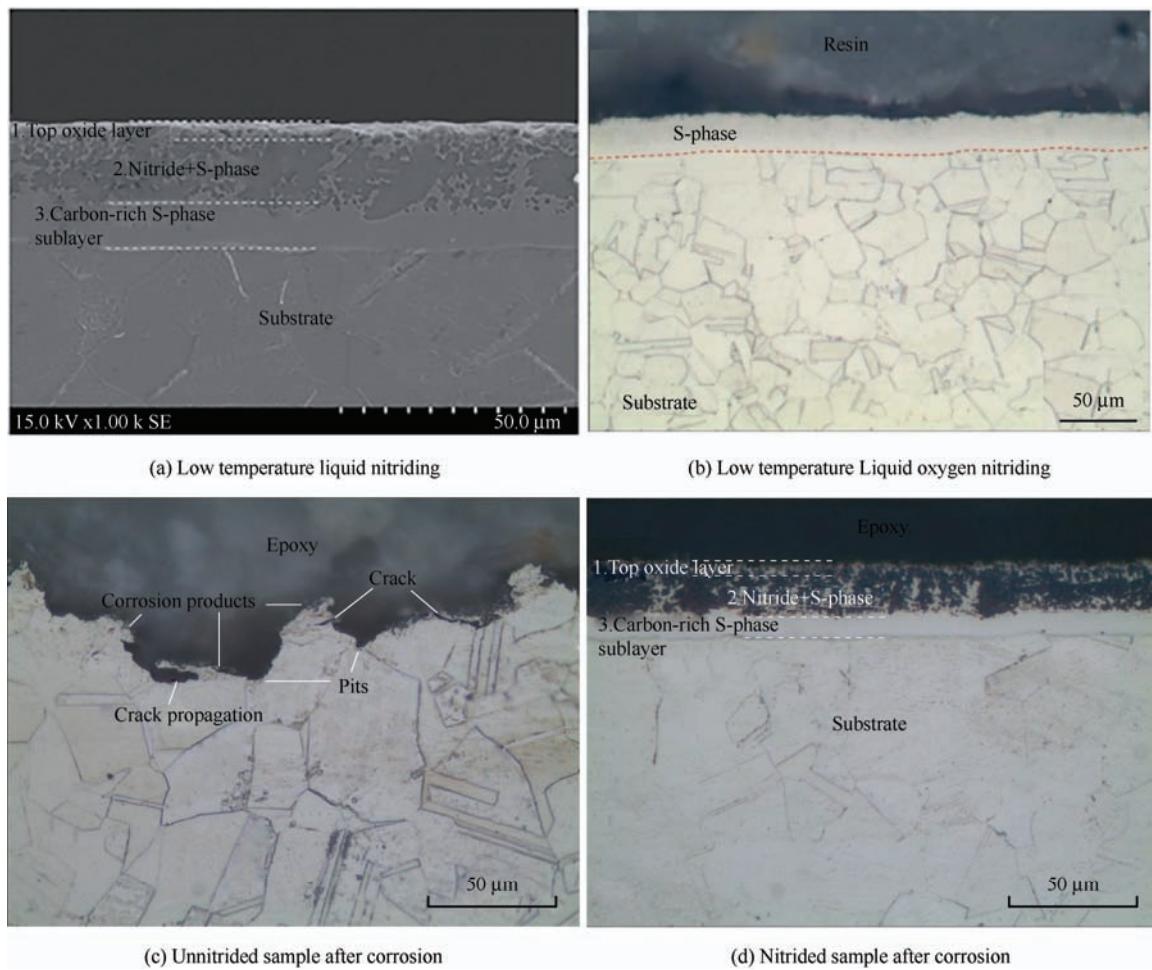
图 8 在 H_2S 溶液中浸泡 720 h 前后样品的横截面^[42-43]

Fig. 8 Cross section of the sample before and after 720 h immersion in H_2S solution^[42-43]

2.2 表面涂层技术

等离子体渗碳、渗氮或碳氮共渗等化学热处理技术能显著提高金属在 $\text{CO}_2 / \text{H}_2\text{S}$ 环境下的耐蚀性，但处理后管道的脆性增大，难以面对油气开采时的冲蚀环境。管道涂层技术不仅能将腐蚀介质与基底阻隔开，还可以减少管内壁的磨损，是在油气开采过程中一种对管道防护极其实用的措施。

Ni-P 涂层在酸性环境中由于次磷酸根离子的形成而表现出比多晶涂层更高的耐腐蚀性，因此在油气开采腐蚀领域受到了广泛的关注^[12]。无涂层的 L360 钢暴露在 $\text{H}_2\text{S} / \text{Cl}^-$ 环境 1 440 h 后表面会发生严重腐蚀，如图 9a 所示，在钢表面产生尺寸超过 50 μm 的腐蚀坑。而涂敷 Ni-P 涂层后腐蚀速率被大幅降低，镍溶解形成腐蚀产物 NiS 与 Ni_3S_2 ，腐蚀产物附着在涂层外表面，抑制了腐蚀介质与化学镀层的直接接触，稳定的 NiO 与 $\text{Ni}(\text{OH})_2$ 钝化膜在腐蚀介质的渗透中起到屏蔽与阻挡的作用，二者共同作用降低了腐蚀速率，暴露于 $\text{H}_2\text{S} / \text{Cl}^-$ 环境 720 h 后，基底上仅产生几微米深的点蚀，在 1 440 h 后点蚀才转变为均匀腐蚀^[11]。同时，在高温高压 $\text{CO}_2 / \text{H}_2\text{S} / \text{Cl}^-$ 环境中 Ni-P 涂层仍能表现出优异的耐蚀性^[12]，硫化物在腐蚀路径的传质过程中与涂层发生反应而被耗尽，其余少量的腐蚀介质能够穿透腐蚀产物层的保

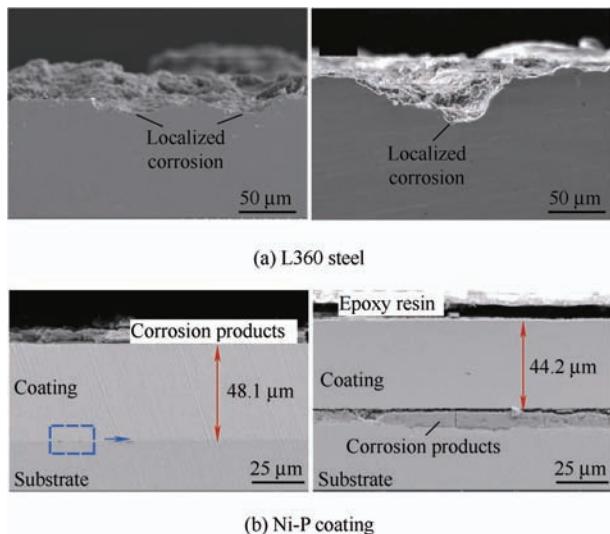


图 9 L360 钢与 Ni-P 涂层在 60 °C 暴露于 $\text{H}_2\text{S} / \text{Cl}^-$ 720 h 及 1 440 h 后的截面形貌^[11]

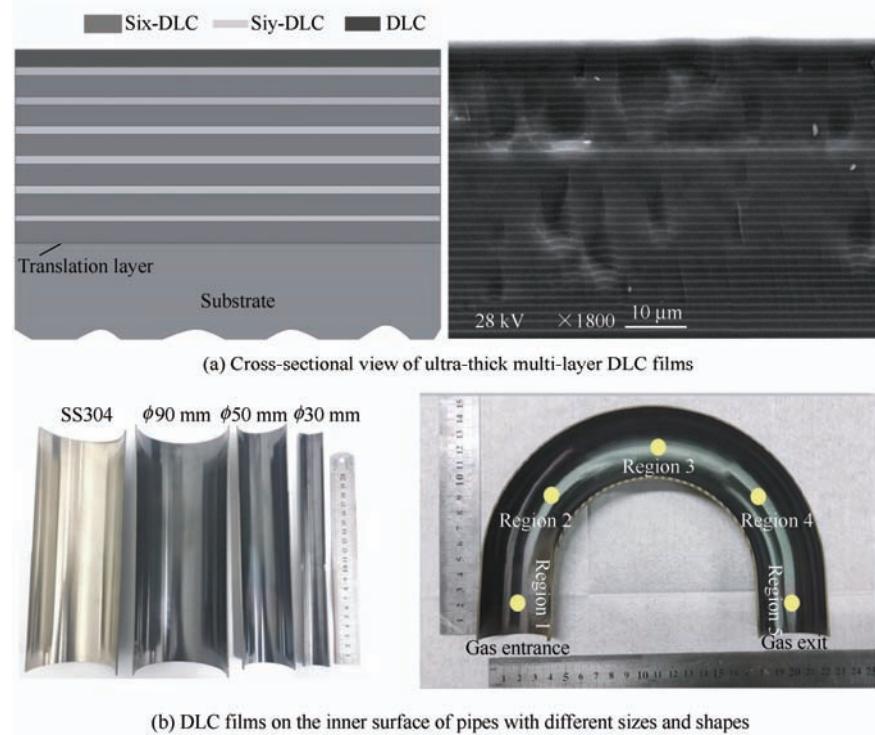
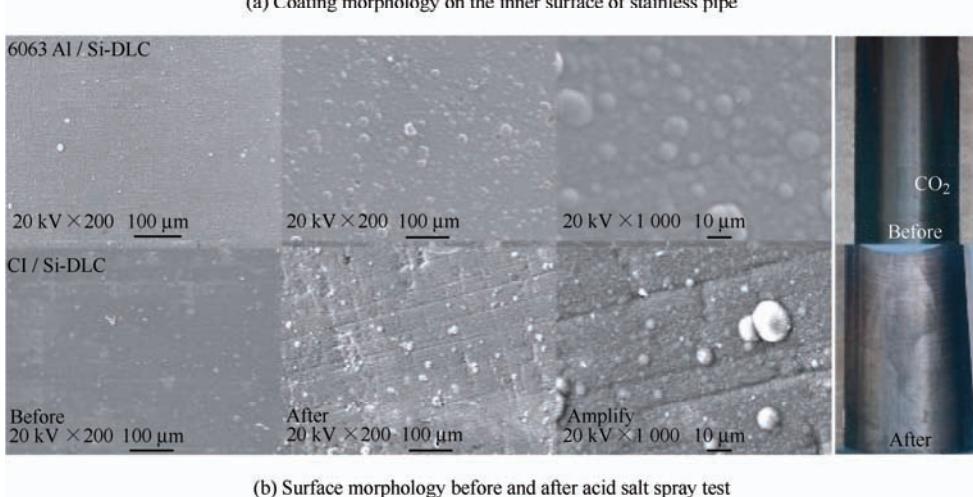
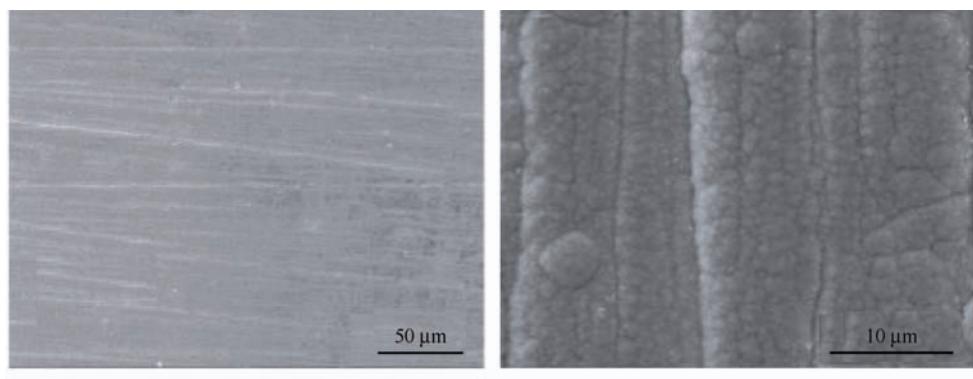
Fig. 9 Cross section morphology of L360 steel and Ni-P coating after exposure to $\text{H}_2\text{S} / \text{Cl}^-$ 720 h and 1 440 h at 60 °C^[11]

护渗透到基底诱发点蚀，致密的腐蚀产物层与较长的腐蚀路径相结合，大幅减缓了腐蚀速率，增强了管道在油气开采环境下的耐蚀性。

涂层在减缓基底腐蚀速率方面有着类似于腐蚀产物的作用，通过阻隔腐蚀介质能够减少渗透到基底的腐蚀介质，并且涂层相比于腐蚀产物层更加致密，具有更好的阻隔效果。同时，部分涂层如 Ni-P 涂层在腐蚀过程中能吸收部分腐蚀性离子，从两方面更有效地对基底进行保护。除了 Ni-P 涂层以外，WANG 等^[44]采用高功率二级管激光器在 X70 基底上制备的 Ni-Cr-Mo 涂层在模拟 H_2S 与 CO_2 溶液中也展现出了稳定的防腐性能。DUSHIK 等^[45]通过化学气相沉积制备的硬质 W-C 系沉积层因其 0.02% 的极低孔隙率和钨的良好耐腐蚀性，被视为很有前途的防腐涂层。

2.3 等离子体镀膜技术

虽然涂层技术在 $\text{CO}_2 / \text{H}_2\text{S}$ 环境中展现出了极其优越的耐蚀性，但如何针对油气开采过程中的实际情况在管道内表面制备涂层仍是一个难点问题。通过空心阴极等离子体增强化学气相沉积技术 (Hollow cathode plasma enhanced chemical vapor deposition, HC-PECVD) 在管道内表面沉积的类金刚石碳基薄膜 (Diamond-like Carbon, DLC) 有着高化学惰性且不与酸碱盐发生任何化学反应的性质^[46-48]，在 CO_2 与 H_2S 共存的高温高压气相环境中对管内壁仍具有良好的保护效果。WANG 等^[49]通过压应力与张应力的多层结构设计，成功制备出厚度超过 50 μm 的超厚 DLC 薄膜，并将这种 DLC 薄膜成功沉积在了不同管径的 304 不锈钢管、铝管、铸铁管及 U 型管道的内表面^[50-52]，如图 10 所示。为了评估 DLC 薄膜的耐蚀性，对薄膜进行 480 h 与 720 h 的中性盐雾试验及高温高压 CO_2 下的腐蚀测试，测试发现薄膜表面没有出现明显损伤，如图 11 所示。盐雾试验后的腐蚀形貌表明 DLC 薄膜具有优异的耐蚀性及长效稳定性，通过 F、N 等元素的掺杂能够进一步提高薄膜的耐蚀性^[53-54]。通过 HC-PECVD 技术在管内壁沉积 DLC 薄膜有望成为减缓管道在油气田环境中腐蚀的新方法。

图 10 多层超厚 DLC 薄膜示意图^[49-51]Fig. 10 Schematic diagram of multi-layer ultra-thick DLC film^[49-51]图 11 管内壁 DLC 涂层腐蚀前后形貌图^[47-48]Fig. 11 Morphology of DLC coating on the inner wall of the pipe before and after corrosion^[47-48]

2.4 金属管道的合金化

将金属管道合金化可以提高管道的耐蚀性, Ni、Cr、Mo、Ti 等元素的掺杂可以有效减缓金属的点蚀和应力腐蚀开裂^[55-58], 元素掺杂后管道的腐蚀形貌会发生变化, 在腐蚀过程中生成更致密的腐蚀产物从而提高管道的耐蚀性。研究者通过研究不同元素含量的合金钢后发现, 在模拟油气开采的 CO₂ / H₂S 环境中, Cr 在腐蚀产物中会以 Cr(OH)₃ 的形式富集^[59], Ni 基合金钢的腐蚀产物中出现 NiS 与 Ni 的氧化物^[60], 元素的掺杂改变了腐蚀产物的形貌与致密性, 钛微合金化后的低碳钢腐蚀后会形成更加均匀致密的内外层薄膜^[61], 腐蚀产物致密性的增加提高了其对腐蚀介质扩散的阻碍能力从而使耐蚀性提高。

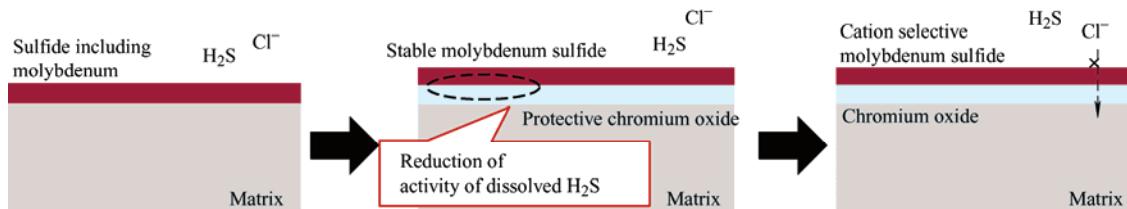


图 12 合金钼对 Ni-Cr-Mo-Fe 合金在 H₂S-Cl⁻环境中耐腐蚀性的作用示意图^[62]

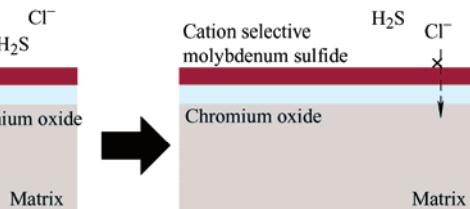
Fig. 12 Schematic diagram of the effect of alloy molybdenum on corrosion resistance of Ni-Cr-Mo-Fe alloy in H₂S-Cl⁻ environment^[62]

2.5 缓蚀剂

注入缓蚀剂是油气开采中一种经济简单的抑制腐蚀方法。LIU 等^[64]系统研究了四种含有不同杂原子的双(苯并咪唑)衍生物对 N80 钢在 H₂S 溶液中的缓蚀作用后, 发现缓蚀剂与管内壁间稳定的吸附单层能减缓管道的阳极溶解和阴极还原反应。缓蚀剂的缓蚀效果与其吸附性能密切相关, 通过吸附在管内壁上来阻止腐蚀介质与管壁的接触, 起到抑制腐蚀的效果^[65-66]。因此, ZHUOKE 等^[67]为了提高缓蚀剂的吸附性能进行了一系列的尝试, 并通过合成曼尼希碱得到了含噻唑环的双曼尼希基 TZBM。TZBM 分子中的 N 和 O 原子包含一对孤电子, 这些孤电子可以进入铁的杂化轨道形成配位键, 并建立一个稳定的六元环结构使 TZBM 牢固地吸附在管道表面。TZBM 吸附在 Fe 表面的示意图如图 13 所示。

然而由于缓蚀剂对环境的潜在污染, 其大规模应用受到了限制, 因此无毒环保的环境友好型缓蚀剂受到了广泛关注, 研究者通过对种子、叶子和果实等植物提取物的缓蚀性能进行研究, 发现了香蕉皮提取物、石榴皮提取物及柑橘皮提取物在 HCl 与 H₂SO₄ 的酸性环境中的缓蚀作用^[68-70]。在这基础上

高。目前, 研究者已经开发了各种 Ni-Cr-Mo-Fe 合金并应用于油气井中, 其中 Mo 的加入能显著提高合金在 CO₂ / H₂S 环境下的耐蚀性。Mo 元素在腐蚀过程中会生成腐蚀产物硫化钼, 与硫化镍与硫化铁不同, 硫化钼具有良好的阳离子选择性, 一方面可以抑制氯离子的溶解反应, 另一方面可以降低硫化膜内的 H₂S 活性来促进氧化铬膜的形成, 从而减缓合金的点蚀与应力腐蚀开裂^[62-63], 合金钼对 Ni-Cr-Mo-Fe 合金耐腐蚀性的作用示意图如图 12 所示。由于油气管道的服役环境极其苛刻, 除了良好的抗 CO₂ / H₂S 腐蚀能力以外, 还要求管道具有优良的力学性能, 同时兼顾生产的经济性, 这是未来合金钢管道的研究热点。



ZHANG 等^[71]进一步发现了柑橘皮在 CO₂ / H₂S 共存卤水溶液中对钢的腐蚀抑制作用。然而, 虽然现在发现的环保型缓蚀剂种类多样, 并都在 CO₂ / H₂S 的酸性环境中具有一定的缓蚀效果, 但对环保型缓蚀剂在模拟油田环境下的高温高压 CO₂ / H₂S 环境下的抑制效果研究很少。油田中温度、pH 值、含水率及流速等外在因素的变化, 对其缓蚀效果的

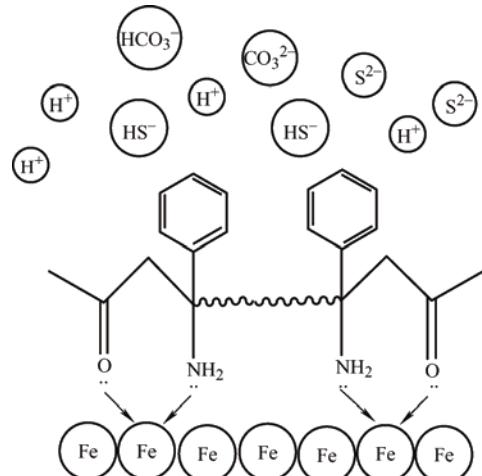


图 13 TZBM 分子吸附机理示意图^[67]

Fig. 13 Schematic diagram of TZBM molecular adsorption mechanism^[67]

影响也缺乏相关的研究。因此,环境友好型缓蚀剂的开发及其在模拟实际油气田环境下的缓蚀效果将是未来的热门研究领域。

3 结论与展望

在油气开采环境下,由多种腐蚀介质与外界因素共同影响的协同腐蚀是油气管道中长期存在的问题。经过近几十年的研究, CO_2 、 H_2S 、 Cl^- 等腐蚀介质的腐蚀机理及离子间的协同腐蚀已经形成了一套完整的腐蚀理论体系,通过模拟实际工况下存在的条件,各种外界因素对腐蚀过程的影响趋势与机理得到了统一的理论。然而由于油气田环境的复杂性与多变性,对于实际工况下的腐蚀环境没有统一的定论,不同因素间的协同作用研究还不够全面。

在管道防护方面,目前的多种防护手段展现出良好的防护效果,比如在高温高压 $\text{CO}_2/\text{H}_2\text{S}$ 环境下仍具有优异耐蚀性的 Ni-P 涂层,通过 HC-PECVD 在管内壁制备的超厚多层 DLC 薄膜以及在植物中提取的环境友好型缓蚀剂,但是对于不同因素影响下的防护技术还缺少全面的测试。基于上述研究现状,未来油气开采环境下管道的腐蚀与防护研究应关注以下两个方面:

(1) 在现有研究的基础上,针对实际工况下的腐蚀因素进行大量试验研究,深入研究协同腐蚀过程中的促进与抑制关系。

(2) 完善现有的防护技术,深入研究各类防护技术在模拟油气田实际工况环境中的防护效果,并确定油气田环境中存在的各类外界因素对现有防护技术的影响。

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