海洋工程装备

滩涂环境 SRB 对涉海管线镁阳极腐蚀影响现状与展望

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摘要：介绍了海洋滩涂环境的特点及其与海底泥土的区别，分析了该环境下微生物腐蚀的发生情况。微生物腐蚀被认为是自然界中最具有侵略性的因素之一，也是目前引起管线破坏失效最主要的因素之一。详细介绍了微生物，尤其是 SRB 引起的管线腐蚀的相关动态，主要涉及 SRB 对氢渗透、失效涂层、缺陷处局部腐蚀、阴极保护的影响。同时，对镁阳极在滩涂环境中的突然失效，以及 SRB 对镁阳极等材料腐蚀严重性等问题进行了总结和分析。最后，提出了滩涂环境中 SRB 的存在对镁合金的影响及研究前景。根据滩涂环境自身的特殊性，研究 SRB 的存在对滩涂环境中镁阳极性能和油气管线安全运行的影响尤为重要。

关键词：海洋滩涂环境；微生物腐蚀；镁合金；硫酸盐还原菌；腐蚀与防护

中图分类号：TG172　　**文献标识码：**A　　**文章编号：**1672-9242(2021)12-0051-08

DOI：10.7643/issn.1672-9242.2021.12.009

Current Status and Prospect of Influence of SRB on the Corrosion of Magnesium Anodes of Buried Pipeline in Mudflat Environment

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ABSTRACT: This paper described the characteristics of the marine mudflat environment and its difference from submarine mud, and analyzed the occurrence of microbiologically influenced corrosion in this environment. Microbiologically influenced corrosion was considered as one of the most aggressive factors in nature, which was also one of the most important factors causing pipelines failure. This paper introduced the research trends of pipeline corrosion caused by microbiologically influenced

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收稿日期：2021-04-21；**修订日期：**2021-07-19

Received: 2021-04-21; **Revised:** 2021-07-19

基金项目：国家自然科学基金（42076043，41376003）；中国科学院战略性先导科技专项（XDA13040405）

Fund: Supported by the National Natural Science Foundation of China (42076043, 41376003) and the Strategic Priority Research Program of the Chinese Academy of Sciences (XDA13040405)

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引文格式：张杰, 兰啸, 王佳, 等. 滩涂环境 SRB 对涉海管线镁阳极腐蚀影响现状与展望[J]. 装备环境工程, 2021, 18(12): 051-058.

ZHANG Jie, LAN Xiao, WANG Jia, et al. Current status and prospect of influence of SRB on the corrosion of magnesium anodes of buried pipeline in mudflat environment[J]. Equipment environmental engineering, 2021, 18(12): 051-058.

corrosion in detail, especially about SRB. It mainly focused on the influence of SRB on hydrogen penetration, failure coatings, local corrosion at defects and cathodic protection. At the same time, the sudden failure of magnesium anodes in the current mudflat environment and the serious corrosion of SRB on magnesium anodes and other materials was summarized and analyzed. The influence and research prospect of SRB existing on magnesium alloys in the mudflat environment was proposed. According to the special mudflat environment, it was particularly important to carry out the research on the influence of SRB on magnesium anode performance, which was even important about the safe operation of oil and gas pipelines.

KEY WORDS: marine mudflat environment; microbiologically influenced corrosion; magnesium alloy; SRB; corrosion and protection

随着海上油气开发的发展，涉海油气管线日益增多，其安全问题也变得尤为重要。这些金属管线处于海泥、海水、滩涂等不同的环境中，不可避免地遭受到各种腐蚀，进而引起管线泄漏等重大安全问题，造成的间接经济损失和社会影响无法估量。因此，如何防止和减缓管道的腐蚀问题是科研工作者面临的重要研究课题。

1 滩涂环境下的腐蚀

1.1 滩涂环境

滩涂环境作为湿地的一种，是位于海岸带受海洋潮汐周期性或间歇性影响的淤泥质湿地[1-2]。滩涂环境在海洋环境中具有独特的生态特征，是一种陆地、海洋、大气间动态相互作用的特殊环境，与海底泥土有本质区别。海底泥土为非均匀的固、液两相电解质体系，金属材料在其中的腐蚀通常为缺氧状态下进行的厌氧腐蚀。滩涂泥是一种由固、液、气三相组成的、极为复杂的、不均匀的多相腐蚀介质；受周期性潮汐变化的影响，含氧量比海底泥土含氧量更丰富；湿度、温度和盐度等随着潮汐发生显著变化。

海洋滩涂环境腐蚀是自然环境腐蚀的一部分，更是海土腐蚀的重要组成部分[3]。土壤腐蚀（包括海土腐蚀）是影响我国管道运行安全的主要因素[4]，其不均匀的物理化学性质为管道内金属的电化学腐蚀创造了条件[5]。

1.2 与海底泥土区的区别

在海泥的研究中，海底沉积物的腐蚀性更受人们关注。有研究发现[6]，在不同区域、不同深度的海泥中，金属的腐蚀速度相差好几倍，厌氧细菌的存在甚至会使埋地管线穿孔。然而，以往对海泥的研究都忽视了滩涂海泥，没有把它作为一种特殊的腐蚀环境和介质进行单独研究，甚至认为金属在滩涂海泥中的腐蚀规律与在海底泥中的腐蚀规律完全一样，这是极其错误的。因为滩涂环境的含水量、含盐量、透气性与普通的陆地土壤和海泥环境有本质区别。有研究发现[7]，近岸海底的厌氧细菌含量更高，这也注定金属管线在滩涂环境中会遭受更严重的微生物腐蚀破坏。但由于滩涂的组成和性质受地理、水文等各种因素的影响较大，往往会造成腐蚀进程复杂多变，难以控制与模拟[8-10]，这也使该区域金属腐蚀的研究甚少。

1.3 研究现状

二十世纪八十年代，我国对滩涂环境进行了详细调查[11-12]，但对滩涂腐蚀性的调查较少[13-14]。由于滩涂环境的特殊性，对材料在滩涂环境中的腐蚀评价和海土腐蚀性能试验的研究更是少之又少。我国海泥腐蚀专家季明棠认为，滩涂海土腐蚀是不同程度的氧去极化腐蚀和厌氧条件下微生物腐蚀的交混过程[15]。薛超波等[16]指出，滩涂环境中硫酸盐还原菌的检出率为 100%，含量很高，数量分布在 9.00×10^4~9.00×10^6 MPN/g（湿重）。在滩涂环境下，厌氧菌等微生物极易繁殖，且在不同的区域和季节中，其含水量差异显著，极易造成局部微观腐蚀电池和宏观腐蚀电池，从而加速金属的腐蚀失效。

2 微生物腐蚀

全世界每年因微生物腐蚀引起的直接损失高达 300~500 亿美元[17]。Fathy 等[18]认为产油井 75%以上的腐蚀和埋地管线 50%以上的腐蚀都是由细菌，特别是 SRB 的活动引起的。由于缺乏对生物腐蚀和生物污损过程的了解，各种设施都是在面临严重的问题或现象后才被正确诊断。实际上，预先采用保护性的方法比失效后再进行修复来的更经济[19]。微生物腐蚀被认为是自然界中最具侵略性的因素之一[20]，也是目前导致管线破坏失效最主要的因素之一[21-24]。SRB 导致的管线腐蚀已经引起了广泛的关注[25]，目前的研究主要集中在以下几个方面。

1）SRB 对氢渗透的影响[25-29]。研究人员发现，海泥中 SRB 的存在加速了氢进入管线[22,26]，增加了应力腐蚀敏感性[26]，导致极化电流增加[28]。同时，SRB 代谢活动产生的 H_2S 和 S^{2-}可以通过加速 H_0 的生成促进氢快速进入金属[28-30]。

2）失效涂层下 SRB 存在引起的管线腐蚀[31-33]。失效涂料下存在的电解液为 SRB 的繁殖提供了适宜的条件[31]，从而促进了微生物腐蚀的加速发生。在含

SRB 的薄液层中，失效涂层下的管道腐蚀是由微生物腐蚀和钢铁表面膜层的协同作用引起的[34]。

3）SRB 的活动促进了缺陷处的局部腐蚀[35-37]。埋地管线处于贫氧和厌氧交替状态，SRB 代谢产生的硫化物和 Cl^-协同作用加速了局部腐蚀，导致管线严重腐蚀和失效[36]。在含 SRB 的介质中，局部腐蚀是埋地输油管线腐蚀的主要形式。金属表面的生物膜和多孔 FeS 产物层是引起局部腐蚀的主要原因[36]，其在金属基体表面形成具有腐蚀性的细胞团簇和 SRB 生物膜，从而促使了局部腐蚀的发生[38]。

4）SRB 对管线在阴极保护或施加阴极极化下的影响[39-41]。研究发现，当阴极保护电位达到−1.10 V(vs. SCE)时，SRB 仍保持一定的生物活性[42]；当阴极保护电位达到−1.00 V(vs. CSE)时，SRB 生物膜引起的局部点蚀仍然存在。阴极保护电位越负，管线钢在 SRB 存在下越容易发生氢损伤[43]。

3　镁阳极的腐蚀

镁阳极因其电位负和驱动电压大等优点，被广泛应用于滩涂环境中埋地管线的阴极保护。然而，在实际工程应用中，工程人员发现镁阳极的电流效率往往偏低。有研究者认为这是由于镁阳极发生严重自腐蚀，局部腐蚀的持续扩展导致阳极颗粒的剥蚀脱落所致[44]。也有观点认为是由于镁阳极与其他金属接触，或表面覆盖腐蚀产物部分与未覆盖产物部分组成电偶腐蚀[45]，第二相或杂质元素的存在引起的微电偶腐蚀所致[46]。

中海油的调查报告指出，某地一设计寿命为 20 a 的管道镁阳极严重失效，实际使用了 2 a 就失去了作用。然而，挖出的镁阳极却依然有 70%的剩余（见图 1）。调查认为，阳极失效是阳极表面的腐蚀产物不导电、不脱落造成的[47]。但是，这个原因不足以造成设计寿命和实际寿命的差异如此巨大，必定有其他因素的参与，首先要考虑的便是微生物腐蚀的影响，它导致了埋地管道和线缆中 50%的故障[48]。特别是 SRB 引起的腐蚀，由 SRB 引起的钢铁材料的微生物腐蚀占腐蚀总损失的 50%以上[49]。Li[50]等对厦门海域挂样 8 a 的金属锈层进行分析，发现 SRB 是腐蚀产物表面生物膜的优势种群，证实了 SRB 在长期微生物腐蚀中的重要性。因此，研究对镁阳极腐蚀性能的影响具有典型代表性，可以得到许多具有普适性的结论。

图 1　镁阳极腐蚀严重照片
Fig.1 Photo of severe corrosion of magnesium anode

国内外关于镁合金和 SRB 腐蚀的研究较少，不同研究者甚至得出了相反的结论。例如，研究发现 AZ91 材料表面在含 SRB 培养基中形成生物膜[51]，生物膜的存在显著降低了镁合金对 Cl^-的腐蚀敏感性[52]，但同时 SRB 又能通过阴极去极化加速镁合金表面的微电偶腐蚀[50-53]。Starosvetsky J[54]等研究发现，当 SRB 存在时，镁铝合金比纯铝腐蚀更严重。另有研究表明，镁具有内在的抗菌杀菌能力，但目前尚不清楚镁诱导杀菌的确切机制[55]。一些研究者将细菌失活归因于合金的降解速率[56]；另有一些研究者将其归因于碱度[57-59]，他们认为，发生在镁腐蚀表面附近的碱化对周围生物有害，碱性 pH 值的增加可导致细胞死亡[59-60]。Feng[61]等却认为镁对微生物的杀灭机理来源于 Mg^{2+}和 OH^-的协同作用，而不单单是碱度。因为他们发现，只有 Mg^{2+}和 OH^-结合在一起才能实现对细菌的完全杀灭，而单独一种离子或 $Mg(OH)_2$沉淀都不能完成杀灭过程。可见，关于 SRB 对镁的腐蚀机理尚无公认的结论。由于滩涂环境的特殊性，虽然对牺牲阳极在陆地及海上的腐蚀性能已经有了相应的测试和国家标准，但结果和原理并不完全适用于滩涂环境中。

4　SRB 对镁阳极腐蚀研究的展望

4.1　SRB 生物膜对镁阳极的影响

前面论述了国内外埋地油气管线的腐蚀防护研究，研究者更多关注的是管线自身的腐蚀问题，而对管线钢提供保护的镁阳极在实际环境中的腐蚀评价没有涉及。事实上，在滩涂海泥埋地管线的阴极保护中，镁阳极是否正常运行严格关系到管线安全。如果镁阳极由于 SRB 的影响出现异常失效，在实际工程中就会出现前文提到的重大工程问题。而且，镁阳极一旦失效，对于整个输油管路都是致命的，其造成的危害远远超过管线本身发生局部腐蚀造成的危害。研究发现，近岸海底和河流入海处的厌氧细菌含量较高[7]。加上滩涂环境本身具有的特殊性，研究 SRB 对该环境下镁阳极性能的影响对油气管线的安全运行就显得尤为重要。

研究 SRB 对镁阳极的影响，首先要关注 SRB 在镁阳极表面形成的生物膜对镁阳极的影响。SRB 前期在金属表面的附着和后期生物膜的形成受各种因素的影响，如环境因素[62]，微生物的物理、化学特性[63-64]，金属基底的表面特征和微结构[65]。因此，研究 SRB 在滩涂环境下对镁阳极性能的影响，必须综合考虑上述因素。有研究发现，生物膜会降低缓蚀剂的有效性[66]。SRB 生物膜会导致金属表面形成局部阳极和阴极区

域，促进阳极反应速率的提高[67]，造成孔蚀和缝隙腐蚀[68-69]等，这些都是加速金属腐蚀的因素。另有研究表明，SRB生物膜能够降低镁阳极对Cl^-的腐蚀敏感性[51]，其表面金属硫化物的形成会对金属起到一定的保护作用[70]，这些又是抑制腐蚀的因素。上述研究说明，SRB生物膜对镁阳极的影响，在生物膜的不同发展阶段和变化的外部条件下，可能会有明显的差别，甚至是相反的结果。因此，研究SRB对镁阳极性能的影响，必须结合滩涂环境的具体环境参数，综合考虑各种因素进行分析。

4.2　“饥饿”状态下SRB对镁阳极的影响

目前，对SRB和埋地管线腐蚀的研究是建立在有足够碳源作电子供体的情况下进行的[71]。然而，在实际的滩涂环境镁阳极的周围，SRB往往没有丰富的碳源可以利用[72]。在有机碳耗尽的情况下，SRB能将从氧化钢铁中获得的电子通过表面FeS产物层转移到SRB中[73]；在极端环境下，SRB几乎能够探寻任何能源来维持他们的生命[74]；在营养物质匮乏时，SRB为了生存甚至可以从死细胞中寻找能源[75]。2004年，Dinh等[76]首次在海洋沉积物中分离出可以只利用金属铁作为电子供体的硫酸盐还原菌，发现该菌株对金属的腐蚀速度远高于有机营养型的硫酸盐还原菌。研究认为，SRB能直接通过电子转移获得能量，引起金属材料的严重腐蚀[77-78]，特别是在缺乏有机电子供体的情况下，电化学微生物腐蚀导致的金属腐蚀速率远高于化学微生物腐蚀，即便在淡水环境中，该情况下电化学微生物腐蚀造成的腐蚀破坏比例可达75%~91%[72]。

研究发现，一些SRB菌株具有独特的无机营养能力，可以不经过H_2中间体，直接从金属表面获取电子[79-80]。因此，在一个特定的、物质交换比较困难的滩涂环境中，SRB对镁阳极腐蚀的影响存在相当大的不确定性，SRB在缺少“食物”情况下，会直接从镁表面获取电子吗？其作用和控制机理是什么？这也是我们非常感兴趣的问题。

4.3　SRB代谢产物对镁阳极的影响

要研究滩涂环境中SRB对镁阳极的影响，还要考虑SRB代谢产物对镁阳极的性能影响。然而，目前关于SRB代谢产物对镁的影响鲜有文献报道，笔者通过查阅SRB代谢产物对其他金属的影响研究，发现SRB引起的金属腐蚀受腐蚀产物与生物膜结构性质的影响很大，薄的、较致密的附着膜有保护性，而大块的、疏松的附着膜会增加腐蚀速率[81]。研究发现，SRB释放的硫化物对很多金属有很强的腐蚀性[82-84]，因为硫化物的存在提高了金属的腐蚀敏感性，主要表现在以下方面：1）引起阴极氢还原（阴极去极化）[85]；2）改变局部pH值，引起点蚀[86-87]；3）促进活化溶解[88]；4）具有好的传导性，促进电子转移[89]。然而，研究者认为在某些条件下，保护性的腐蚀产物层能大大抑制金属腐蚀[90]。可见在不同条件下，得出的结论截然不同。Duan等[91]认为硫化物的形成会对电流密度产生明显影响，从而影响腐蚀。在厌氧腐蚀中，SRB代谢产物对调节金属与细菌间的电子流动有重要作用[89]。另外，金属与分散分布的腐蚀产物之间的电偶腐蚀往往会引起更大的腐蚀速度，造成巨大危害[92-93]。因此，系统研究SRB代谢产物对镁阳极性能的影响，探寻SRB代谢产物制约或加速镁阳极性能变化的关键因素，将为提高埋地管线阴极保护镁阳极效率提供一定的理论基础。

5　结语

综上所述，不难发现，虽然SRB是腐蚀研究中最受关注，也是最重要的微生物，但在某些特殊环境，如滩涂环境下的SRB腐蚀尚未得到足够重视。直接以滩涂为研究对象，进行SRB的腐蚀研究十分有限，而关于SRB对滩涂环境镁阳极的腐蚀过程和作用机制更是缺少研究。因此，深入研究滩涂环境中SRB对镁阳极的腐蚀破坏行为和破坏机理，对发展和提高油气输送具有重要意义。

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