

钢铁材料表面酸洗清洁生产展望

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摘 要: 随着现代工业的发展, 钢铁构件的需求日益增大。钢铁构件由于自身表面性质活跃, 在加工、运输及储存过程中不可避免地形成锈蚀层。钢铁材料的锈蚀既对材料的使用性能及寿命造成不良影响, 又导致材料的巨大浪费。为了提高钢铁构件的使用性能及寿命, 需要进行表面处理及防护, 但处理之前必须清除表面锈蚀层。工业酸洗是清除锈蚀层的重要方法之一, 由于酸洗液腐蚀性强, 在钢铁材料表面锈蚀层溶解后, 不可避免地存在着“过酸洗”的现象, 由此引起钢铁材料的浪费及产生过多的污染物, 如酸雾和酸洗废液等。分析了钢铁材料表面酸洗污染物产生的源头, 并从“缓蚀剂添加、工艺参数选择、酸洗设备改进”等 3 个因素, 总结了提高工业酸洗清洁生产水平的策略, 分析了相关的影响因素, 提出以“源头控污”为核心的酸洗清洁生产的概念, 最后指出了提高酸洗清洁生产水平所需要考虑的问题。

关键词: 酸洗清洁生产; 限制性因素; 缓蚀剂; 工艺参数; 酸洗设备; 过程控制

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Prospect of the Cleaner Production of Steel Surface Pickling

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ABSTRACT: With the development of modern industry, the demand of steel products is increasing. Due to the active nature of steel surface, the formation of rust layers is inevitable during surface treatment, transportation and storage. However, the corrosion of steel had negative effects on the performance and service lifetime for the steel materials, and caused huge waste of resources. In order to enhance the performance of steel products and prolong their service lifetime, surface treatment and protection should be considered. However, before surface treatment and protection, the rust layer should be cleaned out. Industrial pickling is one of the common methods for rust removing. Due to the corrosive characteristic of the used pickling liquors, the phenomenon of over-pickling is inevitable, which may cause the waste of metallic matrix and generate pollutants, including acid mist and pickling waste liquor. In this paper, based on the analysis of the origin of pollution, the methods to enhance cleaner pickling level in industry were discussed and summarized, from three aspects of addition of corrosion inhibitors, selection of the suitable technological parameters and improvement of pickling facilities. Additionally, the factors influencing the above three

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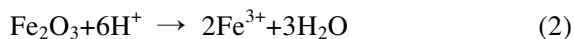
aspects were also discussed. Aiming at enhancing the effect of whole process of pickling industry, the concept of cleaner pickling was proposed, furthermore, the problems which needed to be considered in the future were indicated.

KEY WORDS: cleaner pickling production; limiting factors; inhibitor; technological parameters; pickling facilities; process monitoring

钢铁材料表面性质活跃, 日常运输^[1]、热轧^[2]、表面处理^[3]和储存^[4-5]中不可避免地形成锈蚀层, 导致钢铁构件性能的降低。强酸清洗是去除表面锈蚀层的重要方法, 常见的酸洗液有盐酸^[6-10]、硫酸^[11-14]、硝酸^[15-17]等, 国内盐酸使用较多。虽然强酸酸洗可去除钢铁构件锈蚀层, 但存在一定弊端, 如: 钢铁基体的过腐蚀、酸洗废液(危险废物, 已列入《国家危险废物名录》, 编号 HW34) 过量及酸雾弥漫等, 既损坏钢铁基体, 又造成环境污染^[18]。2014 年中国表观累计钢铁消耗量达 104 622 万吨, 酸洗所需工业盐酸 732.35 吨, 若不采取任何措施, 钢损量达 523.11 万吨(以 0.5% 钢损量计)。酸洗废液处理以末端处理为主, 通过酸碱度调节沉淀金属离子后排放, 会产生大量不稳定污泥, 形成二次污染。本文将从分析传统酸洗行业污染产生的根源出发, 研究主要影响酸洗清洁水平的 3 个因素(缓蚀剂添加、工艺参数选择、酸洗设备优化), 提出酸洗清洁生产概念, 并进一步展望如何提高酸洗清洁生产水平。

1 “过酸洗”产生的原因

钢铁材料的锈蚀层是钢材与空气中氧气接触发生氧化反应而生成的, 主要由 FeO、Fe₂O₃ 和 Fe₃O₄ 组成^[1,19-20]。酸洗液溶解锈蚀层可通过以下方程式表示:



传统酸洗作业方式是在酸洗槽中置入待酸洗构件, 酸浸一段时间后取出并进入下一道工序。但由于锈蚀层性质不一, 且酸洗过程中酸洗液含量随时间变化等原因, 对酸洗终点的判断并不准确。锈蚀层溶解后, 酸洗液会进一步腐蚀材料基体, 产生“过酸洗”现象, 相应的方程式为:



“过酸洗”现象导致了钢铁基体的过腐蚀、

酸洗液过度消耗、酸洗废液过量产生, 是污染物过量产生的根本原因。

2 酸洗缓蚀剂的应用

应用缓蚀剂是缓解“过酸洗”的重要方法。缓蚀剂可分为: 氧化膜型缓蚀剂、沉淀膜型缓蚀剂和吸附膜型缓蚀剂。三者分别在钢材基体表面形成氧化膜、沉积物膜和吸附膜层, 阻隔酸洗液与基体的接触, 减缓“过腐蚀”速率。缓蚀性能越强, “过腐蚀”速率越低。

缓蚀性能可用缓蚀率 η 表征:

$$\eta = \frac{w_0 - w}{w} \times 100\% \quad (5)$$

$$w = w_1 + w_2 \quad (6)$$

式中: w_0 、 w 分别为添加缓蚀剂前后酸洗液质量, w_1 为铁锈质量, w_2 为添加缓蚀剂后“过酸洗”钢损失的质量。

上述公式表达了缓蚀性能强弱与“过酸洗”钢损失量的定量关系, 随着缓蚀率的增加, “过酸洗”钢损量将减少。因此, 缓蚀性能的强弱, 对酸洗工业的清洁程度有重要影响^[21-23]。国内外许多学者研究发现缓蚀性能受多种因素影响, 其中分子结构、水溶性、阳极脱附和复配的影响最为突出。

2.1 分子结构、水溶性对缓蚀效果的影响

缓蚀剂烃基碳原子数越多, 越利于形成厚而紧密的吸附层, 提高缓蚀性能; 但碳原子数超过其最佳范围, 缓蚀剂水溶性则会降低, 影响缓蚀性能^[24]。当然, 水溶性太好, 已吸附的缓蚀剂分子则容易重新溶解至介质中。因此, 缓蚀剂的水溶性也要控制在一定范围内, 才能更好地发挥缓蚀作用。

陈敏等^[25]研究了单环咪唑啉中疏水基团烃基碳链长度对缓蚀性能的影响。研究发现, 疏水基团能极大地提高缓蚀性能, 但当烃基碳原子数少于 12 时, 缓蚀性能明显下降。Ramachandran 等^[26]也发现, 咪唑啉类缓蚀剂中亲水基团碳原子数为 11~19 时缓蚀率最佳, 达 90% 以上; 当碳原子数小

于 10 时, 缓蚀率会迅速降低至 50%。

2.2 复配缓蚀剂对缓蚀效果的影响

由于实际酸洗条件较为苛刻, 单一缓蚀剂的缓蚀效果往往不能满足需求, 因此复配缓蚀剂应运而生。复配体系常为几种缓蚀剂联合使用, 分为无机物与有机物复配体系、有机物与有机物复配体系、无机物与无机物复配体系^[27]。

无机物与有机物复配缓蚀体系, 通过无机离子改变钢材表面电性, 提高有机缓蚀剂的吸附能力, 进而提高体系缓蚀性能。Bouklah 等^[28]研究了碘离子与苯丙烯酰苯衍生物复配的缓蚀性能, 发现缓蚀性能较纯苯丙烯酰苯衍生物明显增加。Amin^[29]和 Umoren^[30]也发现卤素离子的加入, 会强化原有机缓蚀剂的缓蚀性能。Tang 等^[31]研究发现高浓度盐酸下, 碘离子对复配体系的影响存在最佳浓度范围, 当质量浓度大于 8.0 g/L 时, 缓蚀效果减弱。Ebenso^[32]进一步研究了不同卤素原子对复配体系的促进效果, 排序为: $I^- > Br^- > Cl^-$ 。

有机物与有机物复配缓蚀体系, 作用机理表现为 3 种方式: 1) 促进型, 一种有机物 (常为表面活性剂) 的引入增加了另一种有机缓蚀剂的溶解性, 提高了分散性能, 进而提高了缓蚀效果。郭英等^[33]研究了吐温 20 与 PAAC 复配缓蚀剂的性能, 吐温 20 既增加 PAAC 在酸性溶液中的分散度, 也可吸附于铁的表面, 缓蚀效果明显提高。2) 共聚合型, 不同有机物通过聚合作用, 形成更好的物理屏障, 提高缓蚀效果。郭英等^[34]研究了 PAAC 与 PAC 复配体系的缓蚀效果, 通过发生缩合反应, 在酸性条件下形成酰胺基鎓离子并吸附在钢材表面形成保护屏障。3) 互补型, 两种有机缓蚀剂通过相互补充吸附, 提高体系缓蚀性能。喹啉季铵盐与丙炔醇复配体系中, 既通过喹啉季铵盐提高氢的去极化电位保护阴极, 又使丙炔醇分子的双键在金属表面聚合成膜, 连同喹啉季铵盐的吸附膜, 协同提高缓蚀效果。

无机物与无机物复配缓蚀体系, 多使用无机阴离子与高价态无机阳离子复配。Hayashi 等^[35]通过研究 Bi^{3+} 与 Cl^- 的缓蚀性能, 发现 Bi^{3+} 在阴极区还原并吸附于铁表面, 且 Cl^- 在阳极区吸附, 产生协同缓蚀作用。木冠南等^[36]研究了 Ce^{4+} 与 MoO_4^{2-} 的协同缓蚀作用, Ce^{4+} 氧化 Fe^{2+} 为 Fe^{3+} ,

与 MoO_4^{2-} 形成致密膜层, 同时 MoO_4^{2-} 聚合成聚钼阴离子, 与 Ce^{4+} 形成配合物加强吸附膜强度, 提高缓蚀率。

2.3 缓蚀剂阳极脱附对酸洗效果的影响

缓蚀剂在钢铁材料表面吸附是一个动态过程, 涉及吸附和脱附两个方向。脱附速率越低, 缓蚀剂的吸附越稳定, 对钢铁材料基体保护效果越稳定。在实际酸洗过程一些苛刻环节中, 缓蚀剂的吸附稳定性显得尤为重要。缓蚀剂的脱附, 可通过塔菲尔曲线来表征, 表现为阳极部分存在一个腐蚀电流急剧增大的区域。若用微分极化曲线来表征, 则以“脱附峰”的形式呈现^[37-38]。Tao 等^[39]研究了苯三唑类衍生物在低碳钢表面的吸脱附行为, 随着缓蚀剂含量的增加, 脱附不易发生。汪昀华等^[40]进一步研究了缓蚀剂复配体系的阳极脱附行为, 发现复配体系的脱附速率比单组分脱附速率要大得多。

由此可见, 针对缓蚀剂的脱附, 尤其对复配体系, 必须要采取相应措施控制其脱附行为。

3 工艺参数的选择

3.1 材料表面性质对酸洗的影响

钢铁材料表面性质对酸洗过程清洁程度的控制具有指导作用。待酸洗材料表面粗糙度越大, 酸洗阳极过程电子转移活化能越低, 即酸洗速率越快。当表面锈蚀层溶解后, 也更容易出现“过酸洗”现象^[41-42]。因此需对不同表面粗糙度的钢铁材料采取不同的酸洗策略。实际酸洗过程中, 对表面越粗糙的钢铁材料, 在确保酸洗速度的前提下, 可降低酸洗槽中酸洗液温度和浓度, 并提高缓蚀剂浓度减少“过酸洗”所造成的问题。反之, 对表面粗糙度较低的材料, 可采取相反的酸洗策略。

3.2 酸洗温度的影响

温度对酸洗过程的影响表现在对酸洗速度和缓蚀剂吸附性能的影响。温度越高, 酸洗速度越快, 但会加剧缓蚀剂分子的脱附, 加剧“过酸洗”现象。Su 等^[18]发现温度从 30 °C 升高到 60 °C, 活性污泥提取的混合氨基酸缓蚀率从 93.5% 降低至 78.6%。Gopi

等^[43]也发现,温度从 30 ℃提高到 60 ℃,苯并三唑衍生物的缓蚀性能都会出现不同程度的降低,TBTA 的缓蚀率从 41.1%下降至 38.6%,PBTA 的缓蚀率从 53.9%下降至 52.6%,PBTA 的缓蚀率从 70.1%下降至 55.9%。

实际酸洗过程中温度范围变化较大,需尽可能控制在最佳温度范围,以确保缓蚀效率和酸洗速率,以更好地控制“过酸洗”。

3.3 流速对酸洗效果的影响

流速主要影响缓蚀剂吸附性能。流速较小时,液体的流动提高了缓蚀剂分子与钢铁材料的接触时间,促进吸附。流速过快时,较强的冲刷作用会使已吸附的缓蚀剂分子脱附,缓蚀率降低,加剧“过酸洗”现象。Ortega-Toledo^[44]通过不同转速的搅拌,研究了流速对咪唑啉衍生物缓蚀性能的影响,转速为 500 r/min 时,缓蚀效果最佳;转速小于或大于 500 r/min 时,腐蚀速率均会提高。Srisuwan^[45]、Bommersbach^[46]、Ochoa^[47]等的研究均呈现类似规律。Jiang 等^[48]研究发现,随着流速的增加,达到最佳缓蚀率所需的缓蚀剂浓度也随之增加,进而提出高流速下的酸洗对策,即当流速较高时,可通过提高缓蚀剂浓度来降低“过酸洗”影响。

4 设备选型优化酸洗过程

目前酸洗行业普遍采用粗放式管理模式,存在酸洗槽酸雾外泄、酸洗液更换频率高等问题,严重制约着酸洗工业的清洁程度。酸洗设备的优化则能更好地缓解上述问题。

宝钢集团特钢事业部通过对传统酸洗生产线进行密封处理并加装 SCR 烟气脱硝工艺控制酸洗槽酸雾外泄量。同时增加酸洗废液循环系统,通过二级循环(初滤器+旋流分离器和横流颗粒分离器)分离原酸洗废液中的沉淀污泥,回用酸洗废液,减少二次污染^[49]。设备改造前后,各指标对比见表 1。

攀钢成都板材有限公司通过引入酸洗自动控温系统和酸浓度梯级控制系统,把酸洗槽中氢离子浓度控制在最佳范围,确保酸洗速率稳定,更有利于控制“过酸洗”现象。并且通过以上两项改进,大大提高了酸洗卷板质量、缩短了酸洗时间^[50]。

可见,通过改进原有生产设备,引入自动化控制系统,将传统粗放型酸洗系统转变成集约型酸洗系统,能够更准确地把控酸洗终点,减少“过酸洗”现象,使酸洗过程更加环保、清洁。

表 1 酸洗设备优化前后指标对比表

Tab.1 Comparison of indexes before and after optimization of the pickling facilities

生产线	废弃排放标准/(mg·m ⁻³)		有害因素加权平均限制/(mg·m ⁻³)		生产成本/(元/吨)	
	氮氧化物	氟化物	一氧化氮	二氧化氮	能耗	酸耗
原生产线(最高)	195	3.18	14	3.5	51.38	101.5
新生产线(最高)	67	0.80	3	1.5	45.29	83.9

5 展望

酸洗行业作为传统重污染行业,产污量较大,所产生的污染物至今以末端治理为主,虽也有部分企业采用了资源回收的措施,但因市场限制,环境经济效益有限。目前,清洁生产审核工作在很多行业都已经实施,是减轻环境污染、提高资源利用效率的最佳手段。将清洁生产的“全过程控制”的思维运用到传统酸洗行业中,制定酸洗清洁生产审核标准,从源头控污将是未来钢铁酸洗行业的发展趋势。

在此笔者提出酸洗清洁生产概念:酸洗清洁生

产是指不断采取改进措施、采用绿色、高效缓蚀剂、选择合适工艺参数、优化酸洗设备等措施,将节能减排的概念运用于酸洗的全过程,减轻酸洗过程中的过腐蚀、酸洗废液的产生量大、酸雾弥漫等问题,以减轻或消除对人类健康和环境的危害。未来酸洗清洁生产水平的提高应重视以下 4 个方面。

1) 控制全过程。从“添加缓蚀剂、工艺参数选择、设备选型优化”等全过程进行控制。

2) 研制绿色缓蚀剂。对绿色缓蚀剂进行改良、复配,开发出缓蚀效率高、稳定性强且经济可行的新型绿色缓蚀剂。

3) 优化工艺、设备。借鉴国内外酸洗清洁生

产改造的成功案例,不断地优化原有工艺参数和设备选型,亦将对提高酸洗行业清洁生产水平产生推动作用。

4) 落实指标。落实酸洗行业清洁生产评价指标、经济评价指标、环境评价指标,让持续酸洗清洁生产做到有迹可循。

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