ABSTRACT

NACE MR0103 "Materials Resistant to Sulfide Stress Cracking in Corrosive Petroleum Refining Environments"[1] was developed by Task Group 231 to provide a standard set of requirements for materials used in sour petroleum refinery equipment. In the past, NACE MR0175[2], "Sulfide Stress Cracking Resistant Metallic Materials for Oilfield Equipment", was frequently referenced for this equipment, even though refinery applications were outside the scope of MR0175. The process used to develop MR0103 is described, followed by a review of the requirements in the standard accompanied by highlights of the differences between MR0103 and the previous and current versions of MR0175.

摘要

NACE MR0103“腐蚀性石油精炼环境中抗硫化物应力开裂材料” 是由任务小组 231 开发的，目的是为酸性石油精炼设备中使用的材料提供一套标准要求。过去，该设备经常引用 NACE MR0175 “油田设备抗硫化物应力开裂金属材料”标准，尽管炼油应用不在 MR0175 的范围之内。本文描述了用于开发 MR0103 的过程，然后回顾了标准中的要求，并强调了 MR0103 与 MR0175 以前和当前版本之间的差异。

INTRODUCTION AND DOCUMENT HISTORY

In 1975, NACE issued standard MR0175, "Sulfide Stress Cracking Resistant Metallic Materials for Oilfield Equipment", to cover requirements for materials resistant to sulfide stress cracking (SSC) in sour oilfield environments. Although the scope of MR0175 includes only oilfield equipment and associated facilities (including gas production and treatment), the lack of similar standards for other industries has compelled many users in those industries to reference MR0175 for materials destined for “sour” applications. Although the process conditions that constitute the non-oilfield “sour” environments are often quite different from those defined in MR0175, the material and material condition requirements have proven to be fundamentally on target.

介绍及文献历史

1975 年，NACE 发布了 MR0175 标准 “油田设备耐硫化物应力开裂金属材料”，以满足在酸性油田环境中耐硫化物应力开裂材料的要求。虽然 MR0175 的范围仅包括油田设备和相关设施(包括天然气生产和处理)，但由于其他行业缺乏类似的标准，迫使这些行业的许多用户在使用“酸性”材料时参考 MR0175。虽然构成非油田“酸性”环境的工艺条件往往与 MR0175 中定义的有很大差异，但材料和物质条件要求已被证明基本符合目标。

In the late 1990’s, the NACE T-1F-1 task group, now called Task Group (TG) 081, began working on a complete rewrite of MR0175 that included a number of fundamental changes. One of the most significant proposed changes was the expansion of the scope of the document to include chloride stress corrosion cracking (SCC), based upon the fact that most oil and gas production streams contain chlorides in sufficient levels to cause SCC in susceptible alloys. As such, the proposed rewrite included maximum temperature limits for all materials that are susceptible to chloride SCC. For example, the rewrite proposed that the temperature limit for S31600

(type 316 stainless steel) be set at 60°C (140°F) maximum. The proposed changes would mean that MR0175 would be less suitable for use in many applications, including those in petroleum refineries, where chloride ion concentrations tend to be low enough that chloride SCC isn't a common concern.

在 1990 年代后期，NACE 的 T-1F-1 任务组，现在称为任务组(TG) 081，开始对 MR0175 进行完整的重写，其中包括一些根本的改变。最重要的变化之一是扩大了文件的范围，包括氯化物应力腐蚀开裂(SCC)，这是基于这样一个事实，即大多数石油和天然气生产流中含有的氯化物含量足以导致易受影响的合金发生 SCC。因此，提议的改写包括了所有易受氯化物 SCC 影响的材料的最高温度限制。例如，重写建议将 S31600（316 不锈钢类型）的温度极限设置为最大 60°C（140°F）。提议的更改将意味着 MR0175 不再使用于一些应用中，包括在石油精炼厂中的应用，在这些应用中，氯离子浓度往往足够低，以至于氯化物 SCC 不再是普遍关注的问题。

Initial discussion regarding the proposed changes to MR0175 and the potential development of a refinery-specific standard covering materials for sour environments occurred during the 1997 Fall Committee Week T-8 Information Exchange session. Further discussions, including review of drafts of proposed document sections, were held at subsequent T-8 Information Exchange sessions and at several Task Group (TG)T-8-25 ("Environmental Cracking") meetings. At Corrosion/2000, it was decided that a T-8-25 Work Group (T-8-25a) would be formed to develop a sulfide stress cracking document. This Work Group was eventually formed in June 2000 as TG (Task Group) 231 under the current NACE technical committee structure. TG 231 is administered by STG (Specific Technology Group) 34 "Petroleum Refining and Gas Processing" and sponsored by STG 60 "Corrosion Mechanisms".

1997 年秋季委员会周 T-8 信息交流会议期间，就 MR0175 的拟议修改和针对酸性环境的炼油厂专用覆盖材料标准的发展进行了初步讨论。在随后的 T-8 信息交流会议和几个工作组(TG)T-8-25("环境裂缝")会议上进行了进一步的讨论，包括审查拟议文件部分的草案。在腐蚀/2000，决定成立一个 T-8-25 工作组(T-8-25a)来开发一份硫化物应力开裂文件。这个工作组最终在 2000 年 6 月在当前的 NACE 技术委员会结构下成立，名为 TG (Task Group) 231。TG 231 由 STG(特定技术小组)34"石油精炼和气体处理"管理，并由 STG 60"腐蚀机制"赞助。

The task group's writing approach was to borrow pertinent concepts and requirements from the current and proposed versions of MR0175, and modify them as needed to create a new standard that would meet the needs of the oil refining industry. For example, the resulting document utilized the alloy grouping philosophy that is used in what is now MR0175-20033, but did not implement environmental limits such as H2S partial pressures, temperature limits, pH restrictions, etc. Materials and material condition requirements are based upon a mix of MR0175-2002 and MR0175-2003 requirements and refinery-specific experience. Because of this approach, there are paragraphs in MR0103 that are identical to corresponding paragraphs in one or both versions of MR0175, whereas in other instances, the requirements in MR0103 have been modified to better suit the needs of the oil refining industry. The final result is a document that differs from previous and current versions of MR0175 in the following ways:

任务小组的编写方法是从 MR0175 的当前版本和议案版本中借鉴了相关的概念和要求，并根据需要对其进行修改，以便创建一个新的标准，用以满足炼油行业的需要。例如，结果文件使用了 MR0175-2003 3th 的合金分组原理，但没有实施环境限制，如 H2S 分压、温度限制、pH 限制等。材料和材料条件要求是基于 MR0175-2002 和 MR0175-2003 的要求和炼油厂的具体经验。由于这种方法，MR0103 中有些段落与 MR0175 的一个或两个版本的相应段落完全相同，而在其他情况下，MR0103 中的要求已被修改以更好地适应炼油工业的需要。最终得到的文档与 MR0175 之前和当前版本有以下不同:

• The refinery standard guidelines for determining whether an environment is "sour" are quite different from the sour environment definitions provided in previous and current versions of MR0175.

确定环境是否为“酸性”的精炼厂标准指南与MR0175以前和当前版本中提供的酸性环境定义有很大不同。

(也就是说对“酸性环境”的确定，两个标准的定义有很大的不同；

• The refinery standard does not include environmental restrictions on materials.

炼油标准不包括对材料的环境限制。

（材料的环境？？

• Materials and/or material conditions are included in the refinery standard that are not listed in previous and/or current versions of MR0175.

材料和/或材料条件包含在炼油标准中，这些材料在MR0175的以前和/或当前版本中没有列出。

• Materials and/or material conditions are included in previous and/or current versions of MR0175 that are not listed in the refinery standard.

材料和/或材料条件包含在先前和/或当前版本的MR0175中，但未列在炼厂标准中。

• Because welding is prevalent in refinery piping and equipment, extra emphasis is placed upon welding controls in several material groups, most notably the carbon steels.

由于焊接在炼油厂管道和设备中很普遍，所以特别强调了几种材料组的焊接控制，最明显的是碳钢。

The document was developed using the approved NACE work process. Various sections were drafted, reviewed at Corrosion and Fall Committee Week meetings, and then finalized based upon the feedback that was received. The "final" draft was sent out for formal letter ballot in mid-July 2002. This initial ballot resulted in 4 negative votes and 17 affirmative votes with comments. The document was modified to address the negative votes and other comments, and was sent out for reballot in January 2003. The reballot passed with a 97% affirmative vote after negative vote resolution. The MR0103 standard "Materials Resistant to Sulfide Stress Cracking in Corrosive Petroleum Refining Environments" was published in mid-April 2003.

MR0103 标准“耐腐蚀性石油精炼环境中硫化物应力开裂的材料”于 2003 年 4 月中旬发布。

Following is an overview of the document, including discussion of pertinent differences among MR0175-2002, MR0175-2003, and MR0103.

Both MR0175 and MR0103 include sections that describe the applicability of each of the Standards. Within each of these sections there are sub-sections that describe the material and environmental factors that affect susceptibility of materials to SSC and also provide guidelines to the user on how the Standard should be applied. It is extremely important to note that in both MR0175 and MR0103 the user is responsible for determining and judging whether the environmental conditions are such that the material requirements of the Standard should be applied.

MR0175 和 MR0103 都包括描述每个标准适用性的部分。在每个章节中都有描述影响材料对 SSC 敏感性的材料和环境因素的子章节，也为用户提供了如何应用标准的指导方针。非常重要的是，在 MR0175 和 MR0103 中，用户有责任确定和判断环境条件是否符合标准的材料要求。

One of the key differences between the MR0175 and MR0103 Standards lies in the guidelines addressing the environmental conditions under which SSC is likely to occur. This difference between the upstream (oil and gas production) and downstream (refining and gas processing) environments was one of the principal reasons why NACE STG 34/TG 231 decided to write the MR0103 Standard. MR0103 is more focused on a broader range of sour environments conditions experienced in downstream process units.

MR0175 和 MR0103 标准之间的一个主要区别在于，这些准则处理了可能发生 SSC 的环境条件。上游(石油和天然气生产)和下游(精炼和天然气处理)环境之间的这种差异是 NACE STG 34/TG 231 决定编写 MR0103 标准的主要原因之一。MR0103 更关注在下游工艺装置中经历的更广泛的酸性环境条件

The MR0175 definition of sour service environments in upstream processes is very well known and understood, having remained essentially unchanged for almost 30 years. In the 2003 version of MR1075 the environmental conditions likely to cause SSC are described in Paragraphs 1.4.1 and .4.2 with sample calculations in Appendix A. Simply summarized, these conditions consist of a partial pressure of H2S in the wet gas phase of a gas, gas condensate or crude oil equal to or exceeding 0.0003MPa abs (0.05 psia). For gas systems there is a low-pressure cut-off (i.e., total system pressure below which SSC is not expected to occur) of 0.45 MPa abs (65 psia) and for multiphase phase systems the low-pressure cut-off is 1.83 MPa abs (265 psia), (with other conditions applying).

MR0175 对上游过程中酸性应用环境的定义已经广为人知，并且已经基本保持了 30 年的不变。MR1075 2003 版的酸性环境条件是描述在段落 1.4.1 SSC 和.4.2 抽样计算附录 a 中简单的总结, 这些条件包括湿性 H2S 的气相分压的天然气、凝析油或原油等于或超过 0.0003 mpa abs (0.05 psia)。对于气体系统，低压截止值(即系统总压力低于该值时预计不会发生 SSC)为 0.45 MPa abs (65 psia)，而对于多相系统，低压截止值为 1.83 MPa abs (265 psia)(其他适用条件)。

The MR0175 definition of sour service has also been widely and successfully applied by users in many downstream facilities either directly in company specifications and practices or indirectly via the application of API equipment specifications such as API RP 610[4], 617[5] and 618[6]. However, for downstream applications many users, engineering contractors and suppliers have over the years developed their own practices on how and when MR0175 material requirements should be applied. These practices have ranged between:

MR0175 对酸性应用的定义也被用户广泛成功地应用于许多下游设施，直接应用于公司的规范和实践中，或通过 API 设备规范(如 API RP 6104、6175 和 6186)的应用而间接应用。然而，对于下游应用，多年来，许多用户、工程承包商和供应商已经就如何以及何时应用 MR0175 材料要求制定了自己的实践。这些做法包括:

• No application at all, irrespective of H_2S level since some downstream users have considered MR0175 strictly applicable to upstream applications;

完全不应用，无论 H2S 的影响如何，因为一些下游用户认为 MR0175 是严格适用于上游应用的，

• Application of MR0175 material requirements to any process containing H_2S, including trace levels in services with no free water present.

MR0175 材料要求在任何含 H2S 的过程中的应用，包括在没有自由水存在的服务中痕量水平。（无论液体还是气体介质）

In the new MR0103 Standard an attempt has been made to develop consensus guidelines on what constitutes sour service in downstream units based on:

在新的 MR0103 标准中，人们试图根据以下原则，就下游装置中什么是含硫服务达成共识:

• Users plant experience and practices;

用户的使用习惯和经验

• Existing NACE and industry recommended practices and reports (i.e. NACE RP0296[7], 8X194[8], 8X294[9], API Publication 581[10]);

现有的NACE和行业推荐做法和报告

• A fundamental understanding of atomic hydrogen generation in the sour service corrosion reaction and the subsequent rate of hydrogen flux into the process-contacted steel i.e., combined effects of pH, H_2S and HCN.

基本了解酸性腐蚀反应中的原子氢生成，以及随后与过程接触的钢中氢通量的速率，即 pH、H2S 和 HCN 的复合作用。

A significant difference between upstream and downstream sour environments is that in many refinery sour water environments dissolved ammonia is present which increases the pH thereby。

上游酸性环境和下游酸性环境的一个显著区别是，在许多炼油厂酸性水环境中存在溶解氨，从而提高酸碱度。

increasing the solubility of H2S, which in turn increases the bisulfide ion concentration and corrosivity. Ammonium bisulfide corrosion in these high pH environments generates a relatively high rate of hydrogen flux. Furthermore, the presence of cyanides at an elevated pH further aggravates the degree of atomic charging and hydrogen flux into the steel by poisoning the surface reaction that results in a stable and protective iron sulfide scale from forming.

增加了 H2S 的溶解度，从而增加了二硫离子浓度和腐蚀性。二硫化铵腐蚀在这些高 pH 环境产生相对高比率的氢通量。此外，氰化物在 pH 值升高时的存在进一步加重了原子电荷和氢通量进入钢的程度，通过毒害表面反应，导致稳定和保护性的硫化铁垢形成。

The outcome of the consensus approach, embodied in MR0103, has resulted in the following guidelines (with additional explanation in parenthesis) on what constitutes a sour enough service in downstream units to justify the application of the Standard's material requirements (Note: the presence of a free water phase is a prerequisite for aqueous corrosion and SSC):

（自由水相的存在是水腐蚀和SSC的先决条件）

- >50 ppmw dissolved H_2S in the free water (recognition that significant levels of dissolved H_2S can result in SSC even in low pressure systems), or
- A free water pH < 4 and some dissolved H_2S present (recognition that in low pH environments significant charging of materials with atomic hydrogen can take place irrespective of H_2S level), or
- A free water pH > 7.6 and > 20 ppmw hydrogen cyanide ion (HCN) and some H_2S dissolved in the free water (recognition that at high pH the HCN ion is stable and results in significant charging of ferritic materials by poisoning the formation of a protective iron sulfide scale), or
- >0.0003 MPa abs (0.05 psia) partial pressure H_2S in a process with a gas phase (based on historical MR0175 definition of sour service, without low-pressure cut-offs).

以下是该文件的概述，包括讨论 MR0175-2002、MR0175-2003 和 MR0103 之间的相关差异。

• The procedure may only be used to weld a base metal of the same specification, grade, and class as that of the PQR specimen. In other words, a procedure qualified on ASTM A516 Grade 70 plate material could not be used to weld ASTM A516 Grade 60 plate material, ASTM A105 forgings, or ASTM A216 Grade WCC castings, even though all are within the same ASME Section IX P-No. 1 category.

•该程序只能用于焊接与 PQR 试样相同规格、等级和等级的母材。换句话说，一个符合 ASTM A516 70 级板材的程序不能用于焊接 ASTM A516 60 级板材、ASTM A105 锻件或 ASTM A216 级 WCC 铸件，即使它们都符合 ASME 第 IX 节 P-No。1 类。

• The maximum CE and micro-alloying element contents of production material must be controlled to values less than or equal to those of the PQR specimen.

生产材料的最大 CE 和微量合金元素含量必须控制在小于或等于 PQR 试样的值。

• The heat input used during production welding must not deviate from the heat input used during creation of the PQR specimen by more than 10% lower or 25% higher. For the shielded metal arc welding (SMAW)

process, the maximum bead size and the minimum length of weld bead per unit length of electrode used in creation of the PQR specimen can be imposed as an alternate requirement in the WPS.

焊接生产过程中使用的热输入不得与 PQR 试样制作过程中使用的热输入相差超过 10%或超过 25%。对于保护金属电弧焊(SMAW)过程，在创建 PQR 样品时使用的每单位长度焊条的最大焊缝尺寸和最小焊缝长度可以作为 WPS 的替代要求。

• Preheat and interpass temperatures must be at least as high as those utilized in production of the PQR specimen.

预热和过渡温度必须至少与 PQR 样品生产中使用的温度一样高。

• If preheat was not utilized for the PQR specimen, the maximum base metal thickness of production weldments must not be allowed to exceed the thickness of the PQR specimen.

如果没有对 PQR 试样进行预热，生产焊件的最大母材厚度不得超过 PQR 试样的厚度。