

Guidelines for Avoiding Sulfidation (Sulfidic) Corrosion Failures in Oil Refineries

API RECOMMENDED PRACTICE 939-C
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Contents

	Page
1 Scope	1
2 Normative References	1
3 Terms, Definitions, Abbreviations, and Acronyms	1
3.1 Terms and Definitions	1
3.2 Abbreviations and Acronyms	3
4 Basics of Sulfidation Corrosion.....	4
5 Location of Sulfidation Corrosion	7
6 Effects of Process and Material Variables on Corrosion Rates	8
6.1 Introduction	8
6.2 H ₂ -free Sulfidation.....	8
6.3 H ₂ /H ₂ S Corrosion	11
7 Practical Guidelines for Avoiding Sulfidation Corrosion Failures	12
7.1 General.....	12
7.2 Existing Units and Components	12
7.3 New and Replacement Components	18
8 Limitations of Current Knowledge Base.....	19
9 Incidents	20
Annex A (informative) Failure Experience Summary	22
Annex B (informative) Sulfidation Corrosion Prediction Tools	24
Annex C (informative) Corrosion Data for Carbon Steel Piping with Higher and Lower Si Contents	36
Annex D (informative) Overview of Sulfidation Corrosion Throughout Refinery Units.....	40
Annex E (informative) Simplified Inspection Checklist for Refinery Piping and Equipment in Sulfidation Service	44
Bibliography	48
Figures	
1 NPS 8 Carbon Steel Piping Failed Due to Sulfidation Corrosion (H ₂ Free)	5
2 Corroded Carbon Steel Sight Glass Nipple	5
3 FCC Fractionator Bottoms Carbon Steel Piping Operating at 150 psig (1 MPa) and 650 °F to 700 °F (340 °C to 370 °C)	6
4 FCC Fractionator Bottoms Carbon Steel Piping Shown in Figure 3 Operating at 150 psig (1 MPa) and 650 °F to 700 °F (340 °C to 370 °C)	7
5 Summary of Reported Failures by Type, Number of Reported Instances, and Percentage of the Total	21
B.1 Modified McConomy Curves (0.6 % Sulfur Content) (USC Units)	26
B.2 Modified McConomy Curves (0.6 % Sulfur Content) (SI Units).....	26
B.3 Couper-Gorman H ₂ /H ₂ S Curves for Carbon Steel for Both Naphtha and Gas Oil	27
B.4 Couper-Gorman H ₂ /H ₂ S Curves for 1.25Cr-0.5Mo Steel for Both Naphtha and Gas Oil	28
B.5 Couper-Gorman H ₂ /H ₂ S Curves for 2.25Cr-1Mo Steel for Both Naphtha and Gas Oil	29
B.6 Couper-Gorman H ₂ /H ₂ S Curves for 5Cr-0.5Mo Steel for Both Naphtha and Gas Oil	30
B.7 Couper-Gorman H ₂ /H ₂ S Curves for 7Cr-0.5Mo Steel for Both Naphtha and Gas Oil	31
B.8 Couper-Gorman H ₂ /H ₂ S Curves for 9Cr-1Mo Steel for Both Naphtha and Gas Oil	32

Contents

	Page
B.9 Couper-Gorman H ₂ /H ₂ S Curves for 12Cr Steel (Same for Both Naphtha and Gas Oil)	33
B.10 Couper-Gorman H ₂ /H ₂ S Curves for 18Cr 8 Ni Steel (Same for Both Naphtha and Gas Oil)	33
B.11 Corrosion Rate in H ₂ S/High H ₂ Partial Pressure—All Vapor	34
B.12 Corrosion Rate in H ₂ S/High H ₂ Partial Pressure—Liquid Shifted by a Factor of 6 Lower vs Vapor	34
B.13 Corrosion Rate in H ₂ S/H ₂ Vapor—Low H ₂ Partial Pressure (High H ₂ Partial Pressure— All Vapor Curves Adjusted by Experience)	35
C.1 Corrosion Rate vs Si Content for FCC Slurry Carbon Steel Piping Failure (Shown in Figure 3 and Figure 4) (Operating Conditions: 150 psig and 650 °F to 700 °F)	37
C.2 Corrosion Rate vs Si Content for FCC Slurry Carbon Steel Piping Failure (Shown in Figure 3 and Figure 4) (Operating Conditions: 1 MPa and 340 °C to 370 °C)	38
C.3 Corrosion Rate vs Si Content for Various H ₂ -free Services (USC Units)	39
C.4 Corrosion Rate vs Si Content for Various H ₂ -free Services (SI Units)	39

Introduction

Sulfidation corrosion, also often referred to as “sulfidic corrosion,” continues to be a significant cause of leaks in piping and equipment within the refining industry. The objective of this recommended practice (RP) is to provide a better understanding of sulfidation corrosion characteristics and give practical guidance to inspectors and maintenance, reliability, project, operations, and corrosion personnel on how to address sulfidation corrosion in petroleum refining operations. Examples of failures are discussed to highlight the common causes. The methods used to control and inspect for sulfidation corrosion are summarized. The data herein are a compilation of information extracted from published technical papers, industry information exchanges (NACE and API), and contributions from several owners/operators. Some refining companies have developed proprietary methods to predict sulfidation corrosion, and these were not made available as part of this effort.

There are two separate and distinct mechanisms of sulfidation corrosion. One occurs where H_2 is present in addition to the sulfidation-causing sulfur species, as is common in many refining processes, such as hydrotreating and hydrocracking. The other occurs in the absence of H_2 (hydrogen free) in processing units that do not employ H_2 as a component of the process. They both are non-aqueous, diffusion-based corrosion mechanisms that occur at elevated temperature. There is considerable debate in the industry as to the correct threshold temperature for hydrogen-free sulfidation, and in a change in this edition, the API 571 threshold of 500 °F (260 °C) for hydrogen-free services is adopted herein. Experience has shown that little significant corrosion will occur at operating temperatures below 500 °F for hydrogen-free sulfidation services without the influence of naphthenic acid corrosion.

Common refinery units in which essentially H_2 -free sulfidation corrosion can occur are the crude/vacuum, fluid catalytic cracker, coker, and visbreaker units. Hydroprocessing and hydrocracking units can experience H_2 -free sulfidation corrosion in their feed sections before the hydrogen is introduced, and in their distillation sections downstream of where the hydrogen is removed. They experience sulfidation in the presence of hydrogen in their reaction sections. This sulfidation in the presence of H_2 is typically referred to as “ H_2/H_2S corrosion” and the minimum temperature is 450 °F (230 °C).

Included in this RP are:

- background to damage mechanisms,
- the most common types of damage observed,
- root causes of sulfidation corrosion,
- methods to predict and monitor the corrosivity of systems,
- materials selection for new and revamped processes, and
- inspection and non-destructive examination (NDE) methods used for detecting sulfidation corrosion.

Materials and corrosion specialists should be consulted for additional unit-specific interpretation and application of this recommended practice.

Guidelines for Avoiding Sulfidation (Sulfidic) Corrosion Failures in Oil Refineries

1 Scope

This recommended practice (RP) is applicable to hydrocarbon process streams with sulfur-containing compounds, without the presence of hydrogen (H₂), which operate at temperatures above approximately 500 °F (260 °C) up to about 1000 °F (540 °C). There is considerable debate in the industry as to the correct threshold temperature for H₂-free sulfidation, and in a change in this edition, the API 571 threshold of 500 °F (260 °C) is adopted herein. Experience has shown that little significant corrosion will occur at operating temperatures below 500 °F (260 °C) for H₂-free sulfidation services without the influence of naphthenic acid corrosion. Mercaptan corrosion, particularly in condensate service, has been reported below this temperature but is not explicitly covered in the Second Edition of API 939-C. For H₂-containing services, the threshold temperature is set at 450 °F (230 °C).

A lower threshold limit for sulfur content is not provided because significant corrosion has occurred in the reboiler/fractionator sections of some hydroprocessing units (which do not contain H₂) at measured sulfur or hydrogen sulfide (H₂S) levels as low as 1 ppm.

Corrosion of nickel (Ni) base alloys in hot H₂S environments is excluded from the scope of this document. In addition, while sulfidation can be a problem in some sulfur recovery units, sulfur plant combustion sections and external corrosion of heater tubes due to firing sulfur-containing fuels in heaters are specifically excluded from the scope of this document.

2 Normative References

The following documents are referred to in the text in such a way, that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any addenda) applies.

API 570, *Piping Inspection Code: In-service Inspection, Rating, Repair, and Alteration of Piping Systems*

API Recommended Practice 571, *Damage Mechanisms Affecting Fixed Equipment in the Refining Industry*

API Recommended Practice 578, *Guidelines for a Material Verification Program (MVP) for New and Existing Assets*

API 579-1/ASME FFS-1, *Fitness-For-Service*, June 2007, Second Edition

API Recommended Practice 584, *Integrity Operating Windows*

ASME SA-516, *Specification for Pressure Vessel Plates, Carbon Steel, for Moderate- and Lower-Temperature Service*

ASTM A106/A106M², *Standard Specification for Seamless Carbon Steel Pipe for High-Temperature Service*

3 Terms, Definitions, Abbreviations, and Acronyms

3.1 Terms and Definitions

For the purpose of this document, the following terms and definitions apply.

¹ ASME International, 2 Park Avenue, New York, New York, 10016, www.asme.org.

² ASTM International, 100 Barr Harbor Drive, West Conshohocken, Pennsylvania 19428, www.astm.org.