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Materials for Sour Service in Refining and Marketing Operations

Group Practice

**BP GROUP
ENGINEERING TECHNICAL PRACTICES**

Foreword

This is the first issue of Engineering Technical Practice (ETP) GP 36-26. This Group Practice (GP) is based on GP 06-20 and is identical to it in technical content. Although the title of this GP implies it is applicable to Refining and Marketing operation only and it is, its content was developed to be applicable to both Exploration and Production operations and Refining and Marketing operations. It is currently under revision and will be republished with content applicable to Refining and Marketing operations only.

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Introduction

Material types

Numerous types of material are used in sour service, including carbon steel, low alloy steels, corrosion resistant alloys, and other alloys. This has resulted in an extensive amount of satisfactory service experience.

Cracking susceptibility and avoidance

Materials need to be chosen with care, and since they are potentially susceptible to various cracking mechanisms, the particular type depends upon the specific material. For satisfactory service, it is therefore necessary to understand both the environmental conditions and the metallurgical condition of the material that gives rise to the maximum resistance to cracking.

Service failures

Despite much satisfactory service experience, the oil industry, including BP, has seen a number of failures caused by exposure to wet H₂S environments, affecting different equipment and spanning many years. Such failures can potentially be very costly and have severe health, safety, and environmental consequences. Some examples of failures are as follows:

Oil flow line HIC failure of carbon steel pipe (BP) - 1972

- a. Subsea sour oil pipe, offshore in the Middle East.
- b. Pipe was NPS 30, X60, which was subarc seam welded.
- c. Pipe was formed from fully killed controlled rolled mild steel plate, whose microstructure exhibited long, thin manganese sulphide inclusions.
- d. Hydrogen induced cracking (HIC) occurred between the manganese sulphide inclusions.
- e. Cracks linked through the plate thickness, resulting in an 89 mm (3 1/2 in) longitudinal crack.

Downhole tubular string SSC failure of alloyed 13% Cr steel (BP) - 2001

- a. Gas production downhole tubulars in an onshore gas field in Louisiana, U.S.
- b. Wells were high pressure/high temperature gas producers, yielding 1 274 000 m³/d (45 MMscf/d) and containing 50 ppm H₂S and 8,7 mol% CO₂ (0,5 psi H₂S, pH 3,5).
- c. Well completion was with an alloyed martensitic 13Cr steel, (13Cr/4Ni/1Mo) 95 ksi strength tubing.
- d. Packerless completion allowed produced fluid to contact the tubing outside diameter (OD).
- e. Tubing failed by sulphide stress cracking (SSC) at localised sites of cold work on the OD (at locations with slip and tong marks).
- f. Gas, water, and sand flowed from the tubing bore to the annulus, resulting in significant erosion of both the tubing and casing.



- g. Tubing was replaced with super martensitic 13Cr 95 ksi 13Cr/5Ni/2Mo that has increased H₂S resistance over the previously used 13Cr/4Ni/1Mo alloy. Care was taken to minimise slip/tong damage.
- h. Casing was repaired with an expandable solid casing patch.

Failure by SOHIC of carbon steel spiral welded pipe (Saudi Aramco) - 1998

- a. Spiral welded pipe can be particularly susceptible to stress oriented hydrogen induced cracking (SOHIC).
- b. SOHIC failures on spiral welded pipe occurred in the Middle East, and SOHIC cracking was found on 3 out of 39 joints.
- c. Residual stresses are very high in spiral welded pipe. The pipe was subject to a high hydrogen charging rate.
- d. Material that suffered SOHIC had a threshold stress of 117 MPa (17 ksi). Nonfailed material had a higher threshold stress of 206 MPa to 241 MPa (30 ksi to 35 ksi).
- e. Conventional longitudinally welded pipes were also present in the line and exhibited HIC but not SOHIC.

Failure by SSC/SOHIC of carbon steel pressure vessel (Unocal) - 1984

- a. Unocal refinery in Lemont, Illinois, with several fatalities.
- b. Vessel was in amine absorber service.
- c. Failure occurred by SOHIC emanating from an SSC crack.
- d. Cracking was initiated at the location of a repair to a stress relieved vessel, which was performed without post weld heat treatment (PWHT).
- e. Other features were a mismatched joint and some internal cladding with Monel alloy 400 nearby.

Responsibility

Responsibility is now placed on the equipment user by both NACE MR0175/ISO 15156 (oil and gas production) and NACE MR0103 (refining) to ensure that materials used in sour service are fit for purpose.

Different oil and gas production and refining standards reflect different operating conditions, with higher pressures and more acid conditions (lower pH) being present in oil and gas production plant, often making conditions more onerous.

General outline of a sour service plan

Because equipment in wet H₂S environments has a propensity to fail, if not properly controlled, it is imperative to have a sour service plan that covers the following:

- a. Initial materials selection that complies with either of the following:
 - 1. NACE MR0175/ISO 15156 (oil and gas production).
 - 2. NACE MR0103 (downstream).
- b. Detailed operational aspects, including environmental conditions and inspection requirements to confirm continued integrity (Annex D).
- c. Additional requirements set by appropriate BP ETPs.



Important issues that are discussed in this GP are as follows:

- a. Distinction between upstream (oil and gas production) and downstream (refining).
- b. Environmental conditions.
- c. SSC resistance of materials.
- d. Stress corrosion cracking (SCC) resistance of materials.
- e. HIC/stepwise cracking (SWC) resistance of materials.
- f. SOHIC and soft zone cracking (SZC) resistance of materials.
- g. Equipment specific requirements.
- h. Fabrication.
- i. Related services (e.g., alkaline/H₂S environments).
- j. In service issues.



1. Scope

- a. This GP provides requirements to avoid environmental cracking of materials used for equipment in sour service (i.e., fluids containing water and hydrogen sulphide [H₂S]).
- b. This GP is supplementary to the following NACE/ISO oil and gas and refining standards:
 1. NACE MR0175/ISO 15156, oil and gas production (upstream).
 2. NACE MR0103, refining (downstream).
- c. Additional BP specific requirements are provided, including other aspects related to cracking but not included in NACE standards.
- d. General corrosion is not covered in this document and is therefore a separate consideration.

2. Normative references

The following referenced documents may, to the extent specified in subsequent clauses and normative annexes, be required for full compliance with this GP:

- For dated references, only the edition cited applies.
- For undated references, the latest edition (including any amendments) applies.

BP

GIS 18-014	Heat Exchanger Tube End Fixing.
GIS 34-101	Axial and Centrifugal Compressors and Expander-Compressors (ISO 10439 or API 617).
GIS 34-102	Integrally Geared Centrifugal Compressors (ISO 10442 or API 672).
GIS 34-103	Packaged Reciprocating Gas Compressors (ISO 13631, Formerly API 11P).
GIS 34-104	Reciprocating Compressors (ISO 13707 or API 618).
GIS 34-106	Rotary Screw Compressors (API 619).
GIS 34-107	Expander-Compressors (API 617).
GIS 34-108	Integrally Geared Compressors (API 617).
GIS 34-201	Centrifugal Pumps (ISO 13709 or API 610).
GIS 34-202	Horizontal Centrifugal Pumps (ASME B73.1).
GIS 34-203	Vertical In Line Centrifugal Pumps (ASME B73.2M).
GIS 34-204	Centrifugal Pumps (ISO 5199).
GIS 34-205	Seal-less Rotodynamic Pumps (ISO 15783).
GIS 34-701	Lubrication, Seal-Oil, and Gas Seal Systems (ISO 10438 or API 614).
GIS 36-102	Hardness Testing, Post Weld Heat Treatment, Stress Relief, and Pickling for Pressure Vessels, Piping, and other Components.
GIS 36-107	Integral Cladding, Weld Overlay, and Limited Loose Lining of Pressure Vessels and Components.
GIS 42-101	Fabrication, Assembly, Erection, and Inspection of Carbon, Carbon Manganese, and Low Alloy Steel Pipework (ASME B31.3).
GIS 42-102	Fabrication, Assembly, Erection, and Inspection of Austenitic and Duplex Stainless Steel, Cupro-Nickel, Nickel Base Alloy, Titanium, and Zirconium Pipework (ASME B31.3).
GIS 43-331	Pipeline Welding (API 1104).



GIS 43-332	Pipeline Welding (ISO 13847).
GIS 43-333	Pipeline Welding (BS 4515-1).
GIS 46-010	New Pressure Vessels.
GP 06-60	Painting of Metal Surfaces.
GP 36-10	Metallic Material Selection.
GP 36-12	Amine Services.
GP 52-10	Insulation.

American Petroleum Institute (API)

API RP 579	Fitness-for-Service.
API RP 945	Avoiding Environmental Cracking in Amine Units.
API Spec 5CT	Specification for Casing and Tubing.

American Society of Mechanical Engineers (ASME)

ASME Boiler and Pressure Vessel Code (ASME Code).
ASME Boiler and Pressure Vessel Code Section IX - Welding and
Brazing Qualifications.

American Society for Non-Destructive Testing (ASNT)

ASNT TC-1A	Personnel Qualification and Certification in Nondestructive Testing.
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American Society for Testing and Materials (ASTM)

ASTM A193/A193M	Alloy-Steel and Stainless Steel Bolting Materials for High Temperature or High Pressure Service and Other Special Purpose Applications.
ASTM A194/A194M	Carbon and Alloy Steel Nuts for Bolts for High Pressure or High Temperature Service, or Both.
ASTM A516/A516M	Pressure Vessel Plates, Carbon Steel, for Moderate- and Lower-Temperature Service.
ASTM A841/A841M	Steel Plates for Pressure Vessels, Produced by Thermo-Mechanical Control Process (TMCP).

British Standards Institute (BSI)

BS EN 10028-3	Flat products made of steel for pressure purposes. Weldable fine grain steels, normalized.
BS EN 10028-6	Flat products made of steel for pressure purposes. Weldable fine grain steels, quenched and tempered.
BS EN 10160	Ultrasonic testing of steel flat product of thickness equal or greater than 6 mm (reflection method).
BS EN 10164	Steel products with improved deformation properties perpendicular to the surface of the product. Technical delivery conditions.
BS EN 10204	Metallic materials. Types of inspection documents.

International Organization for Standardization (ISO)

ISO 6508-1	Metallic materials - Rockwell hardness test - Part 1: Test method (scales A, B, C, D, E, F, G, H, K, N, T).
ISO 11960	Petroleum and natural gas industries - Steel pipes for use as casing or tubing for wells.



ISO 15156	Petroleum and natural gas industries - Materials for use in H ₂ S-containing environments in oil and gas production.
ISO 15156-1	Petroleum and natural gas industries - Materials for use in H ₂ S-containing environments in oil and gas production - Part 1: General principles for selection of cracking-resistant materials.
ISO 15156-2	Petroleum and natural gas industries - Materials for use in H ₂ S-containing environments in oil and gas production - Part 2: Cracking-resistant carbon and low alloy steels, and the use of cast irons.
ISO 15156-3	Petroleum and natural gas industries - Materials for use in H ₂ S-containing environments in oil and gas production - Part 3: Cracking-resistant CRAs (corrosion-resistant alloys) and other alloys.

NACE International (NACE)

NACE MR0103	Standard Material Requirements - Materials Resistant to Sulfide Stress Cracking in Corrosive Petroleum Refining Environments.
NACE MR0175	Petroleum and natural gas industries - Materials for use in H ₂ S-containing environments in oil and gas production.
NACE RP0472	Methods and Controls to Prevent In-Service Environmental Cracking of Carbon Steel Weldments in Corrosive Petroleum Refining Environments.
NACE TM0284	Evaluation of Pipeline and Pressure Vessel Steels for Resistance to Hydrogen-Induced Cracking.

3. Terms and definitions

For the purposes of this GP, the following terms and definitions apply (see NACE MR0175/ISO 15156, part 1, part 2, and part 3, section 3, for full details):

Hydrogen flux

Hydrogen atoms produced by corrosion that may diffuse into the steel, resulting in various damage mechanisms. This species is often referred to as nascent hydrogen and/or H⁰.

Hydrogen flux is defined as a flow of hydrogen per unit area and is typically measured in picolitres (pl) of gaseous hydrogen at 20°C (68°F) per cm² of steel surface, per second (i.e., pl/cm²/s). Hydrogen flux is affected by pH and pH₂S and other factors, such as the presence of cyanides and arsenic.

Pressure

References to pressure in NACE standards are to be considered the design pressure.

pH (measure of acidity/alkalinity)

Minus log of hydrogen ion concentration.

pH₂S (partial pressure of H₂S)

Pressure of H₂S that would be exerted if present alone, at the same temperature, in the total volume occupied by the mixture.

Sour service

Exposure to environments that contain H₂S and liquid water (H₂O) and can cause cracking of materials by the mechanisms addressed in this document.



4. Symbols and abbreviations

For the purpose of this GP, the following symbols and abbreviations apply (see NACE MR0175/ISO 15156, part 1, part 2, and part 3, section 3, for full details):

BOF	Basic oxygen furnace.
CE	Carbon equivalent.
CLR	Crack length ratio.
CSR	Crack sensitivity ratio.
CTR	Crack thickness ratio.
ERW	Electric resistance welded.
FCCU	Fluid catalytic cracking unit.
FFKM	Perfluorontated fluoro elastomer.
FKM	Fluoro elastomer.
FPB	Four point bend.
GHSC	Galvanically induced hydrogen stress cracking.
HAZ	Heat affected zone.
HIC	Hydrogen induced cracking.
HNBR	Hydrogenated nitrile butadiene rubber.
HSC	Hydrogen stress cracking.
IIW	International Institute of Welding.
NBR	Nitrile butadiene rubber.
NDE	Nondestructive examination.
OD	Outside diameter.
PACR	Predicted average cracking ratio.
PTFE	Polytetrafluoroethylene.
PWHT	Post weld heat treatment.
RBI	Risk based inspection.
SAW	Submerged arc welded.
SCC	Stress corrosion cracking.
SOHIC	Stress oriented hydrogen induced cracking.



SSC	Sulphide stress cracking.
SWC	Stepwise cracking.
SZC	Soft zone cracking.
TFEP	Tetrafluoroethylene propylene.
TMCP	Thermo mechanical control process.
UT	Uniaxial tension.
WFMT	Wet fluorescent magnetic particle examination.

5. Factors affecting cracking

5.1. General materials factors

5.2. General environmental factors

5.3. Factors affecting SSC

Maximum acceptable hardness levels to minimise the possibility of SSC cracking are specified in NACE MR0175/ISO 15156 or NACE MR0103 and NACE RP0472.

5.4. Factors affecting SZC

5.5. Factors affecting GHSC

5.6. Factors affecting HIC/SWC and blistering

5.7. Factors affecting SOHIC

5.8. Factors affecting SCC

6. Distinction between upstream (oil and gas) and downstream (refining)

6.1. General

If H₂S conditions vary, peak transient conditions shall be used in design.

6.2. Different environments for upstream and downstream

- Acidity shall be defined.
- Chloride content shall be defined.
- Contaminants (e.g., cyanides, arsenic, and ammonia) shall be reported and considered in material selection.
- Conditions shall be clearly defined if establishing the suitability of a material.
- Changes were made to NACE MR0175 (now NACE MR0175/ISO 15156) that related materials performance more closely to oil and gas environments, particularly for SCC.

6.3. Upstream (oil and gas) NACE MR0175/ISO 15156

- Mechanisms - SCC, HIC/SWC, SOHIC, SZC, and GHSC are included, as well as SSC.

