



Document No.	GP 06-20
Applicability	Group
Date	25 October 2005

Guidance on Practice for Materials for Sour Service

GP 06-20

**BP GROUP
ENGINEERING TECHNICAL PRACTICES**

Foreword

This is the first issue of Engineering Technical Practice (ETP) BP GP 06-20. This Guidance on Practice (GP) is based on parts of heritage documents from the merged BP companies as follows:

British Petroleum

GS 136-1 Materials for Sour Service March 1997 (Amendment 1 – October 2001).

Amoco

A MM-GEN-00-E	Metallic Materials—General—Selection Specification.
A MM-SS-00-P	Metallic Materials—Special Services—Procurement Specification.
A TG-C&T-S&U-G	Tubular Goods—Casing and Tubing—Selection and Use of OCTG—Guide.
A TG-C&T-SS-P	Tubular Goods—Casing and Tubing—Sour Service OCTG—Procurement Specification.
A PN-PLT-SS-E	Piping—Plant—Special Service—Engineering Specification.
A PN-PL-5L-G	Piping—Pipeline—API5L Steel Line Pipe—Guide.
A PN-PL-5LC2-P	Piping—Pipeline—API5L Performance Category 2—Procurement Specification.
A PN-PL-5LC3-P	Piping—Pipeline—API5L Performance Category 3—Procurement Specification.

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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 however, since they are potentially susceptible to various cracking mechanisms, the particular type depending upon the specific material. For satisfactory service therefore, it is necessary to understand both the environmental conditions and also 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. The following are some examples of failures:

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

- Sub-sea sour oil pipe, offshore in the Middle East.
- The pipe was NPS 30, X60 which was sub-arc seam welded.
- Pipe was formed from fully killed controlled rolled mild steel plate, whose microstructure exhibited long, thin manganese sulfide inclusions.
- HIC cracking occurred between the manganese sulfide inclusions.
- Cracks linked through the plate's thickness resulting in a 3 ½ in longitudinal crack.

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

- This was on gas production downhole tubulars in an onshore gas-field, in Louisiana, USA.
- The wells were high pressure/temperature gas producers yielding 45 mmscf/d, containing 50 ppm H₂S and 8,7 mol % CO₂ (0,5 psi H₂S, pH 3,5).
- Well completion was with an alloyed martensitic 13Cr steel, (13Cr/4Ni/1Mo) 95 ksi strength tubing.
- Packerless completion allowed produced fluid to contact the tubing OD.
- Tubing failed by SSC at localised sites of cold work on the OD (at locations with slip and tong marks).
- Gas, water and sand flowed from the tubing bore to the annulus, resulting in significant erosion of both the tubing and casing.
- 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. Also 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 SOHIC.
- b. SOHIC failures on spiral-welded pipe occurred in the Middle East, and SOHIC cracking was found on three out of 39 joints.
- c. Residual stresses are very high in spiral-welded pipe and the pipe was subject to a high hydrogen charging rate.
- d. The material that had suffered SOHIC had a threshold stress of 17 ksi, whilst non-failed material had a higher threshold stress of 30-35 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. This was at a Unocal refinery in Lemont, Illinois with several fatalities.
- b. The 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 carried out without PWHT.
- e. Other features were a mis-matched joint and some internal cladding with Monel alloy 400 nearby.

Responsibility

The 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 the materials used in sour service are fit for purpose.

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

General outline of a sour service plan

In view of the propensity to failure of equipment in wet H₂S environments, if not properly controlled, it is imperative to have a sour service plan which covers the following:

- a. Initial materials selection which complies with either of the following:
 - 1. NACE MR0175/ ISO 15156 (Oil and Gas Production) or
 - 2. NACE MR0103 (Downstream).
- b. Detailed operational aspects, including the environmental conditions and inspection requirements to confirm continued integrity (Annex A.4).
- c. Additional requirements set by appropriate BP ETP specifications.

The following is a list of important issues that are discussed in this document:

- a. Distinction between Upstream (Oil and Gas Production) and Downstream (Refining).
- b. Environmental conditions.



- c. SSC resistance of materials.
- d. SCC resistance of materials.
- e. HIC/SWC resistance of materials.
- f. SOHIC & SZC resistance of materials.
- g. Equipment specific requirements.
- h. Fabrication.
- i. Related services e.g. alkaline/H₂S environments.
- j. In-service issues.

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1. Scope

This GP provides guidance as follows:

- a. Requirements are given to avoid environmental cracking of materials to be used for equipment in sour service i.e. fluids containing water and hydrogen sulfide (H₂S).
- b. This document is supplementary to the NACE 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 given, including other aspects related to cracking, not included in the NACE standards.
- d. General corrosion is not covered in this document and is therefore a separate consideration.

2. Normative references

The following normative documents contain requirements that, through reference in this text, constitute requirements of this technical practice. For dated references, subsequent amendments to, or revisions of, any of these publications do not apply. However, parties to agreements based on this technical practice are encouraged to investigate the possibility of applying the most recent editions of the normative documents indicated below. For undated references, the latest edition of the normative document referred to applies.

American Petroleum Institute (API)

API Spec 5CT	Specification for casing and tubing (ISO 11960).
API RP 579	Fitness for Service.
API RP 945	Guidelines for Avoiding Corrosion and Cracking Problems in Amine Units.

American Society of Mechanical Engineers (ASME)

ASME Boiler and Pressure Vessel Code	
Section IX	Standard for Welding and Brazing Procedures, Welders, Brazers, and Welding and Brazing Operators.

American Society for Non-destructive Testing (ASNT)

ASNT SNT-TC-1A	Recommended Practice for No. SNT-TC-1A.
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American Society for Testing and Materials (ASTM)

ASTM A193/A193M	Standard Specification for Alloy-Steel and Stainless Steel Bolting Materials for High-Temperature Service.
ASTM A194/A194M	Standard Specification for Carbon and Alloy Steel Nuts for Bolts for High Pressure or High Temperature Service, or Both.
ASTM A264	Standard Specification for Stainless Chromium-Nickel Steel-Clad Plate.
ASTM A265	Standard Specification for Nickel and Nickel-Base Alloy-Clad Steel Plate.
ASTM A395/A395M	Standard Specification for Ferritic Ductile Iron Pressure-Retaining Castings for Use at Elevated Temperatures.



ASTM A516/A516M	Standard Specification for Pressure Vessel Plates, Carbon Steel, for Moderate- and Lower-Temperature Service.
ASTM A841/A841M	Standard Specification for Steel Plates for Pressure Vessels, Produced by Thermo-Mechanical Control Process (TMCP).

BP

GIS 34-101	Guidance on Industry Standard for ISO 10439 Axial Centrifugal Air Compressors (API 617).
GIS 34-102	Guidance on Industry Standard for API 672 Integrally Geared Centrifugal Compressors (ISO 10442).
GIS 34-103	Guidance on Industry Standard for ISO 13631 Packaged Reciprocating Gas Compressors (Formerly API 11P).
GIS 34-104	Guidance on Industry Standard for ISO 13707 Reciprocating Compressors (API 618).
GIS 34-106	Guidance on Industry Standard for API 619 Rotary Screw Compressors (ISO 10440-1, DIS 10440-2).
GIS 34-107	Guidance on Industry Standard for API 617 Expanders.
GIS 34-108	Guidance on Industry Standard for API 617 Integrally Geared Process Compressors.
GIS 34-201	API 610 Centrifugal Pumps (ISO 13709).
GIS 34-202	Guidance on Industry Standard for ASME B73.1 Centrifugal Pumps.
GIS 34-203	Guidance on Industry Standard for ASME B73.2M Centrifugal Pumps.
GIS 34-204	Guidance on Industry Standard for ISO 5199 Centrifugal Pumps.
GIS 34-205	Guidance on Industry Standard for ISO 15783 Seal-less Centrifugal Pumps.
GIS 34-701	Guidance on Industry Standard for ISO 10438 Lubrication, Seal Oil, and Gas Seal Systems (API 614).
GP 36-10	Guidance on Practice for Metallic Material Selection.
GP 36-12	Guidance on Practice for Metallic Materials for Amine Service.
GIS 36-102	Guidance on Industry Standard for Hardness Testing, Post Weld Heat Treatment, Stress Relief, and Pickling for Pressure Vessels, Piping, and other Components.
GIS 36-107	Guidance on Industry Standard for Integral Cladding, Weld Overlay, and Limited Loose Lining of Pressure Vessels and Components.
GIS 42-101	Guidance on Industry Standard for Fabrication, Assembly, Erection, and Inspection of Carbon, Carbon Manganese, and Low Alloy Steel Pipework (ASME B31.3).
GIS 42-102	Guidance on Industry Standard for 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	Guidance on Industry Standard for Welding Exceptions for API 1104.
GIS 43-332	Guidance on Industry Standard for Welding Exceptions for ISO 13847.
GIS 43-333	Guidance on Industry Standard for Welding Exceptions for BS 4515.
GIS 46-010	Guidance on Industry Standard for New Pressure Vessels.
GP 06-60	Guidance on Practice for Coating of Metal Surfaces and Equipment.
GP 18-03	Guidance on Practice for Heat Exchanger Tube End Fixing (GS 118-8).
GP 52-10	Guidance on Practice for Materials for Thermal Insulation of Pipework and Equipment (GS 152-1).



British Standards Institute (BSI)

BS EN 10028	Flat product made of steels for pressure purposes – Part 1: General requirements. Part 2: Non-alloy and alloy steels with specified elevated temperature properties. Part 3: Weldable fine grain steels, normalised. Part 4: Nickel alloy steels with specified low temperature properties. Part 5: Weldable fine grain steels, thermomechanically rolled. Part 6: Weldable fine grain steels, quenched and tempered. Part 7: Stainless steels.
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 products – Types of inspection documents.

International Organisation for Standardisation (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 (API Spec 5CT).
ISO 15156	Petroleum and natural gas industries (Oil & Gas) – Materials for use in H ₂ S-containing environments in oil and gas production (NACE MR0175). Part 1: General principles for selection of cracking-resistant materials. Part 2: Cracking-resistant carbon and low alloy steels & the use of cast iron. Part 3: Cracking-resistant CRAs (corrosion resistant alloys) & other alloys.

NACE International (NACE)

NACE MR0103	Materials Resistant to Sulfide Stress Cracking in Corrosive Petroleum Refining Environments.
NACE MR0175	Petroleum and Natural Gas Industries (Oil and Gas) – Materials for use in HS Containing Environments in Oil and Gas Production (ISO 15156).
NACE RP0403	Avoiding Caustic Stress Corrosion Cracking of Carbon Steel Refinery Equipment and Piping.
NACE RP0472	Methods and Controls to Prevent In-Service Cracking of Carbon Steel Weldments in Corrosive Petroleum Refining Environments
NACE TM0284	Test Method-Evaluation of Pipeline Steels for Resistance to Stepwise Cracking.

3. Terms and definitions

For the purposes of this GP, the following terms and definitions apply:

(See NACE MR0175/ ISO 15156 Parts 1, 2, & 3 – Section 3 for full details)

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

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 pico litres (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

Where the NACE standards refer to pressure, this shall be taken as the design pressure.

4. Symbols and abbreviations

For the purpose of this GP, the following symbols and abbreviations apply:

(See NACE MR0175/ ISO 15156 Parts 1, 2 & 3 – Section 3 for full details)

ASCC	Alkaline stress corrosion cracking
CE	Carbon equivalent
CLR	Crack length ratio
CSR	Crack sensitivity ratio
CTR	Crack thickness ratio
ERW	Electric Resistance Welded
FPB	Four point bend
GHSC	Galvanically induced hydrogen stress cracking
HAZ	Heat affected zone
HIC	Hydrogen-induced cracking
HSC	Hydrogen stress cracking
IIW	International Institute of Welding
PWHT	Post weld heat treatment
SCC	Stress corrosion cracking
SOHIC	Stress-oriented hydrogen-induced cracking



SSC	Sulfide stress cracking
SWC	Stepwise cracking
SZC	Soft zone cracking
TMCP	Thermo mechanical control process
UT	Uniaxial tension

5. Factors affecting cracking

5.1. General materials factors

- *Chemical composition including CE.*
- *Thermal history.*
- *Strength.*
- *Hardness.*
- *Microstructure and homogeneity.*
- *Presence and type of non-metallic inclusions.*
- *Stress level (applied & residual, including thermally and mechanically induced).*
- *Effect on the above factors of welding, repairs, and PWHT.*

5.2. General environmental factors

- *Wet $H_2S \rightarrow H^0 \rightarrow H_2$ production*
Nascent hydrogen is produced on the material surface by wet H_2S corrosion reaction, as well as other corrosion mechanisms (e.g. CO_2 corrosion). In many environments, two nascent hydrogen atoms combine to form molecular hydrogen and bubble away from the surface as follows:
$$2H^0 \rightarrow H_2 (\uparrow)$$

However, environments containing dissolved hydrogen sulfide, can inhibit this reaction and allow the H^0 to build up on the surface and then diffuse into the metal. Inside the metal, atomic hydrogen can result in SSC, as well as HIC and its related mechanisms if H^0 recombines to form the more stable molecular H_2 that is a considerably larger and becomes trapped in the metal.
- *pH*
Hydrogen generation is low in neutral solutions (pH 7), but increases at both lower and higher levels of pH.
- *Other contaminants*
Some contaminants, such as As, and CN^- , increase the concentration of H^0 on the surface, likely by inhibiting the formation of H_2 , and, thus, increase hydrogen entry and flux.
- *Velocity*
Protective sulfide films can be damaged by erosion under high velocity conditions and also by cleaning for inspection.
- *Temperature*
Increasing temperature increases the amount of hydrogen by increasing the corrosion reaction rate but can also reduce the damaging effects of absorbed hydrogen in some cases by increasing mobility/diffusion rate through the material (e.g. for carbon and low alloy steels).



5.3. Factors affecting SSC*Mechanism*

SSC occurs under the combined action of tensile stress and corrosion in the presence of water and H₂S. This is a form of HSC. Atomic hydrogen produced by corrosion diffuses into the steel and results in hydrogen embrittlement at high hardness/stress locations. The presence/level of H₂S and presence of sulfide scales increase the amount of atomic hydrogen available for diffusion by 'poisoning' the hydrogen recombination reaction, hence making HSC more likely.

Strength and hardness

High strength steels and areas of high hardness, such as a weld HAZ or areas of high residual stresses from cold work or thermal history, are particularly susceptible to SSC. Steels containing elements that increase hardenability such as C, Cr, Mo, Nb, and V lead to higher strength and susceptibility. Restriction of carbon content and CE is beneficial in restricting strength and hardness. NACE MR0175 indicates that nickel should be < 1% in steels for sour service. There is however evidence that this can be successfully exceeded under some conditions. High strength weld filler metal has suffered SSC in the past and this led to the development of NACE RP0472. Compliance with the specified hardness levels for weldments is achieved in practice by control of weld procedures, including the selection of consumable composition, strength and/or PWHT.

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

Stress

Cracking is promoted by high stress levels. Both applied stresses and residual stresses (e.g. resulting from welding, thermal history, or cold work) need to be taken into account.

Temperature

Maximum SSC susceptibility often occurs at a low or intermediate temperature. For carbon and low alloy steel plus some CRAs (e.g. 13Cr martensitic stainless steel) this can be taken as around ambient conditions (N.B. In some circumstances where lower temperatures can be experienced, e.g. low seabed temperatures, susceptibility to SSC can be increased). However, for a number of CRAs, maximum susceptibility occurs at an intermediate temperature. For example, in the case of duplex stainless steels, maximum susceptibility occurs at a temperature in the range 80°C to 100°C (176°F to 212°F) due to a 'mixed mode' (SSC and SCC) failure mechanism.

Testing – NACE TM1077.

5.4. Factors affecting SZC*Mechanism*

This is a form of SSC, that occurs when the steel contains a local 'soft zone' of low yield strength. Under service stresses, such soft zones may yield producing local plastic strain, thereby increasing the susceptibility to cracking of an otherwise SSC-resistant material. Such soft zones are typically associated with the HAZ of welds in carbon steel.

Key factors

Key factors are hardness differential and localized stress level.

5.5. Factors affecting GHSC*Mechanism*

HSC is cracking that results from the presence of hydrogen in a metal and tensile stress that may be residual and/or applied. Galvanically-induced hydrogen stress



cracking (GHSC) describes cracking in metal/service condition combinations that are not necessarily sensitive to SSC, but that may be embrittled by hydrogen when galvanically coupled as the cathode to another metal that is subject to active corrosion as an anode in the presence of H_2S .

Key factors

Key factors in this type of cracking are potential difference and anode/cathode area relationship.

5.6. Factors affecting HIC/SWC and blistering

Mechanism

Hydrogen atoms diffuse into steel and can collect at inclusions and other discontinuities and combine to form stable molecular hydrogen. The H_2 molecule is considerably larger than H^0 and is too large to diffuse through the metal. Thus, H_2 is trapped and builds up and a pressure is then exerted at the location within the metal. This may lead to laminar cracking in the plane of non-metallic inclusions resulting in HIC or blistering. Transverse cracks can occur between laminar cracks on different planes and such cracking is known as SWC. HIC/SWC cracking does not require the application of an external stress as an internal stress is built up by the accumulated hydrogen pressure.

Steel cleanliness

Historically conventional steels contained a lot of sulphur and phosphorus that contributed to forming non-metallic inclusion. These sites are traps for H^0 to H_2 combination. In some cases blistering tends to form when the hydrogen-trap sites are near the surface. Newer clean steels (ultra low S and P) are now available with significantly better resistance to HIC and blistering.

Microstructure

Steels with banded microstructures and containing anomalous structures are more vulnerable to HIC. Improvements in resistance to HIC have been obtained by normalizing, quench and tempering and manufacturing with the TMCP process.

Product Form

Plate steel is the most susceptible to damage because of the elongated nature of the inclusions. In contrast, seamless pipe and forgings have more rounded inclusions and do not have significant sensitivity to HIC/SWC and blistering.

Testing – NACE TM0284.

5.7. Factors affecting SOHIC

Mechanism

SOHIC consists of a stacked array of small laminar cracks/blisters joined by hydrogen induced cracking that is aligned in the through-thickness direction of the steel as a result of high localized tensile stresses. SOHIC has similarities to HIC/SWC, but also is related to SSC and is typically found in the weld HAZ, though not exclusively so.

Stress effects

Residual and applied stresses play an important role in the production of SOHIC, which differs from the case with HIC. High stresses promote cracking, as also does the presence of stress raising notch-like defects and SSC cracks.

Material factors affecting SOHIC

Some of the newer clean HIC-resistant steels are believed to be more susceptible to SOHIC. This contention is supported by their lower threshold stress in the SSC test. Others, however, have a very high threshold stress, indicative of good SOHIC resistance. A Materials Properties Council (MPC) study showed that

