

THE ENGINEERING EQUIPMENT AND MATERIALS USERS ASSOCIATION

A WORKING GUIDE FOR CARBON STEEL EQUIPMENT IN WET H₂S SERVICE

(DEVELOPED LARGELY FROM OIL REFINERY EXPERIENCE)

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THE ENGINEERING EQUIPMENT AND MATERIALS USERS ASSOCIATION

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FOREWORD

This EEMUA Working Guide has been prepared by a joint working group of members of the Association's Materials & Fabrication (MAT) and Inspection & NDT Technology (INT) Committees. The guide draws on practical experience, largely in oil refineries, of working with equipment in wet H₂S service and aims at giving guidance on all aspects associated with wet H₂S, taking account of process conditions, materials selection, fabrication, repairs and inspection. It is not intended as a Standard or Code of Practice, but as a guide to those involved with wet H₂S environments. It brings together relevant information on the subject, and the intent is that the guide should be applicable to any process plant handling wet H₂S. It should be used in conjunction with the user's own standards to derive a policy for addressing potential wet H₂S problems in new and existing equipment.

Several documents dealing with aspects of wet H₂S service are available. NACE in particular has been very active in this area and has published a number of these:

NACE MR 01 75 has been established for a long time giving guidance on the avoidance of sulphide stress cracking (SSC). Although it is strictly applicable to upstream operations only, many people have used its recommendations more generally to avoid SSC. In particular it defines conditions likely to promote SSC, recommends materials to be used and details their hardness limits.

NACE has recently revised RP 04 72 which is aimed at controlling hardness of welds and heat affected zones (HAZ) for *inter alia* wet H₂S service. This document specifically addresses downstream operations.

In addition to this, the NACE T8 Group Committee on Refining Industry Corrosion has produced a number of documents in the wet H₂S area, such as NACE RP 02 96, and NACE International Publications 8 X 194 and 8 X 294.

More recently the European Federation of Corrosion has extended this approach further and has published a document (Publication No. 16) for upstream operations, which emphasises the importance of the role of pH in determining the likelihood of SSC.

Units

This publication employs SI units, but additionally may include Imperial units where appropriate to common usage. Unless otherwise stated, partial and total pressures are in absolute units.



1. SCOPE

This document summarises existing knowledge and recommended practices for the specification, design, manufacture, inspection and repair of carbon steel equipment in wet H₂S service. Most types of carbon steel equipment are within its scope, both new and used. However, some of the damage mechanisms associated with wet H₂S exposure are essentially confined to equipment manufactured from rolled plate, notably pressure vessels and seam welded piping, hence there is an emphasis in this area.



2. INTRODUCTION

2.1 Damage Mechanisms

The absorption of hydrogen resulting from the corrosion of carbon steel in wet hydrogen sulphide (H_2S) can lead to two main types of problem:

- sulphide stress cracking (SSC)
- hydrogen induced cracking (HIC) resulting from the build up of internal pressure at inclusions and other defects in the steel; this can result in hydrogen blistering, step-wise cracking (SWC) and stress-oriented hydrogen induced cracking (SOHIC).

Typical forms of damage are illustrated in Fig 1.

The severity of hydrogen damage depends on a combination of factors. These include process conditions, materials, methods of construction and operating history.

2.2 Process Conditions

The process conditions leading to cracking involve the presence of an aqueous environment containing dissolved hydrogen sulphide. Sour service with respect to SSC is defined as set out in 3.1 below. Liquid only systems are not addressed but a figure of 50 ppmw H_2S in the water phase is often used, irrespective of system pressure, as a definition of 'wet H_2S ' service. Potential for attack is greatest under the following conditions:

- increasing acidity
- in the presence of cyanides or other species promoting hydrogen permeation
- a combination of high pH and high H_2S concentration.

2.3 Materials Factors

The material quality and condition have an effect on resistance to hydrogen damage: for SSC, the material composition, level of hardness and imposed stress (applied and residual) are all factors which affect the likelihood of cracking; for HIC and SOHIC, steel chemistry, cleanliness and homogeneity affect the likelihood of cracking.

To improve the resistance to hydrogen damage in general, it is preferable to select good quality lower strength grades of carbon steel and to minimise micro-alloying elements and other elements which promote hardenability. This should help avoid undesirable weld and heat affected zone hardness and reduce residual stresses.

For resistance to HIC special low sulphur steels are available to enhance performance, and have been used with success in many applications. Ultrasonic examination and HIC testing are carried out to give an assessment of material resistance to hydrogen damage.

It should be recognised, however, that manufacturing vessels from these materials and employing controlled methods of construction do not guarantee resistance to wet H_2S damage.

In some circumstances, internal cladding or coating has been used to improve resistance to damage.

2.4 Welding and Post-Weld Heat Treatment (PWHT)

Weld procedure qualification should be subject to special attention to avoid high hardnesses. Hardness testing of weldments is necessary.

A hydrogen removal treatment may need to be carried out before welding on equipment that has been in wet H₂S service.

PWHT is beneficial in reducing the likelihood of SSC, and possibly SOHIC, because it reduces residual stresses to a general level of 20–30% of yield and tempers the weld zone microstructure. However, additional stresses from nozzle loadings, internal pressure etc. may locally increase the overall stresses, and under these conditions SSC or SOHIC might still be possible.

2.5 Classification of Risk

Risk can be assessed by taking account of:

- i) materials as installed and their susceptibility to SSC and HIC, and hydrogen loading, leading to a prediction of the probability of cracking
- ii) an evaluation of the consequences of failure.

2.6 In-Service Inspection

It is important to carry out inspection to confirm the integrity of steels operating in wet H₂S service. An inspection schedule should be established based upon risk and operational factors. This should be regularly reviewed in the light of inspection evidence.

It should be noted that since wet fluorescent magnetic particle inspection (WFMPI) of in-service vessels has become more common, the detection and reporting of cracking in pressure vessels in wet H₂S has increased due to the sensitive nature of the test. However, one consequence of this during subsequent operation is believed to be an increase in hydrogen charging rates on prepared surfaces. It may be necessary therefore to apply some means of protecting such surfaces after WFMPI during start up, or to use some alternative inspection method, e.g. external ultrasonics, which does not disturb the partially protective sulphide scale.

3. PROCESS CONDITIONS

The range of process conditions which are relevant to any of the various forms of wet H₂S attack are those which permit a liquid water phase to occur at some stage, including normal operation, start-up, shutdown, and during special operations such as catalyst pre-sulphiding and regeneration.

3.1 Conditions for SSC

Process conditions which promote SSC have been defined by NACE MR 01 75 as below:

- gas systems:** partial pressure of H₂S > 0.0003 MPa (0.05 psi) and total pressure > 0.4 MPa (65 psi)
- multiphase systems:**
- (a) H₂S partial pressure > 0.0003 MPa (0.05 psi) and system total pressure > 1.8 MPa (265 psi) for H₂S concentration in gas phase up to 4 mol %
 - (b) H₂S partial pressure > 0.07 MPa (10 psi) for H₂S concentration in gas phase between 4 and 15 mol %
 - (c) H₂S concentration in gas phase > 15 mol %.

These limits were derived from the analysis of SSC failure data of oil and gas production equipment, most of which would have been manufactured from relatively high strength medium carbon and low alloy steels. The recommendations in the NACE document for avoidance of SSC in all types of steels focus on metallurgical factors, principally heat treatments and hardness (i.e. tensile strength) limits. It is fair to say that application of the document has, over the years, been extremely successful in controlling SSC in upstream production operations, though recent research has suggested that the NACE definitions of sour service may be unduly conservative.

New approaches to defining sour service using calculated in situ pH vs H₂S partial pressures may permit a slightly more relaxed policy towards the application of some materials, particularly for well tubulars (EFC Publication 16). This approach may also affect materials selection and fabrication criteria for refinery equipment in the future.

Application of the NACE MR 01 75 criteria for refinery equipment has been fairly common, even though such equipment is beyond its stated scope. The most common SSC failures in refinery equipment are also associated with components manufactured from relatively high strength medium carbon and low alloy steels, and martensitic stainless steels, e.g.

- valve trims
- internal fasteners
- machinery parts, notably in sour gas compressors
- springs.

Some user companies consider that certain components made from high strength steel remain susceptible to SSC at process conditions below the sour service limits of NACE MR 01 75 particularly when they are subjected to high levels of applied stress.

The next most common cause of SSC in refineries is excessive weld zone hardness, and this problem led to the development of the NACE document RP 04 72, which gives guidance on methods and controls to avoid this and other refinery environmental cracking mechanisms.

Nevertheless, SSC failures in refinery equipment are relatively infrequent, partly because most fabricated pressure-containing items use low strength grades of carbon steels which can often meet the NACE hardness criteria without difficulty (even in the as-welded condition provided that high strength weld consumables are avoided). However, even low strength steels can be susceptible to SSC at very high stresses. Also, many refinery process streams containing wet H_2S operate at total pressures below the NACE MR 01 75 thresholds, particularly the higher thresholds applicable to multiphase systems.

3.2 Conditions for HIC

Process conditions defining safe and unsafe zones for HIC are not fully understood and have proved difficult to determine. In some users' experience, HIC and hydrogen blistering have been more prevalent in refinery equipment in recent years than SSC, and have been observed to occur under a wider range of operating pressures, often well below the NACE MR 01 75 total pressure thresholds. Indeed HIC and blistering have been found in flare systems operating essentially at atmospheric pressure, and even in vacuum distillation overhead equipment operating at negative pressures.

HIC and blistering are often associated with wet H_2S conditions where other chemical species have shifted the solution pH to either the strongly acidic or strongly alkaline condition. The levels of H_2S required to promote HIC and blistering under these low and high pH states are still subject to investigation. However, one figure which has been widely quoted in the literature as a tentative threshold is 50 ppmw H_2S in the water phase. This figure is probably a reasonable one above which special precautions need to be taken, but it should not be seen as an absolute threshold as such.

Other complications in deciding and advising on process limits include the difficulty in obtaining accurate and reliable process data for H_2S and other species, and the knowledge that the operating conditions may not remain within the expected range during service. It is recommended that for initial evaluation the worst-case conditions should be used, including conditions associated with transients such as start-ups, shutdowns, steam-outs, as well as the more predictable "operational upsets" such as low pH condensate in crude distillation overheads.

The other chemical species usually associated with H_2S in generating HIC and blistering are hydrogen chloride, ammonia and cyanides. Hydrogen chloride is most commonly found in crude oil and, to a lesser extent, in vacuum distillation overhead systems where low pH H_2S environments have caused HIC damage in equipment such as seam welded piping, vessels and air cooler header boxes. Ammonia is mainly associated with hydrotreating and hydrocracking plants, and alkaline sour condensates have been responsible for numerous corrosion problems including HIC, especially in reactor effluent condensers and downstream separators. Cyanides are mainly associated with catalytic cracking units and have been widely implicated in HIC and blistering of the associated gas plant equipment, notably absorber-stripper columns, overhead condensers and gas compressor inter- and after-coolers.

A proper classification of the severity of normal and transient process conditions would require detailed information on the effect of variables on hydrogen permeation rate. Whilst some hydrogen permeation data is available in the literature, there is insufficient available on which to build a detailed severity classification at present.

"Severe" process conditions for promoting HIC and blistering would appear to be:

- H_2S above 50 ppm and low pH conditions (below about 5.0)
- H_2S above 50 ppm and high pH conditions (above about 9.0)
- H_2S above 2000 ppm and high pH conditions (above about 7.8)
- H_2S above 50 ppm and cyanides.

Other process variables such as temperature and stream velocity may also be important. High stream velocities, for instance, can prevent semi-protective sulphide films forming and so can result in high sustained rates of hydrogen charging, e.g. at locations of impingement.

