

Project Proposed by IEOT, Panvel

Sub: H₂S serviceability of 13 Cr martensitic stainless steel in oil and gas environment with variation in partial pressure of H₂S, pH and salinity, especially in partial pressure of H₂S and pH regime above 1.5 psi and 3.5 respectively

Introduction and objectives:

Over the last several years, recently-developed high-strength martensitic stainless steel (MSS) oil country tubular goods (OCTG) including modified 13Cr (95, 110, 115 ksi grade) steels have seen more frequent consideration for use in the completion of HPHT deepwater wells and large bore gas wells.

These high-strength MSS fill the gap between conventional 13Cr steel (API 13Cr-L80) and duplex stainless steels with respect to material strength, corrosion and cracking performance, and cost effectiveness. Compared to API 13Cr-L80, these alloys modified with 4~6% Ni and 1~2% Mo and with the control of C (0.03% maximum) offer increased strength with good notch toughness and improved resistance to CO₂ corrosion and chloride pitting at higher temperatures up to 400°F. However, high-strength MSS can still be susceptible to localized corrosion (pitting) and environmentally assisted cracking (EAC) in sour (H₂S-containing) environments.

The proper identification of H₂S serviceability limits of high-strength MSS in sour oil and gas production environments is an important engineering wherein further research work requires to be done. The serviceability limits of 13 Cr steel needs to be studied with variation in partial pressure of H₂S, pH and salinity, especially in partial pressure of H₂S and pH regime above 1.5 psi and 3.5 respectively.

Proposed scope of work and goal/deliverables:

The goal of this collaborative project is to develop (1) a model describing physical chemistry of H₂S and its impact on the corrosion mechanism observed in commonly used oil field materials. (2) This project will focus on development of novel approaches to model phase behavior and obtained results will be correlated with laboratory corrosion and environmental cracking data. (3) The proposed corrosion tests will provide important experimental and theoretical insights into the role of speciation in compressible liquid vapor systems and phase equilibria on relevant corrosion mechanisms.

(4) The program is also designed to provide new data on Sulfide Stress Cracking (SSC) crack initiation in high strength steels under HPHT conditions and compare results with corresponding low pressure conventional test conditions. (5) Such evaluations are expected to provide the rationale for relaxing the very restrictive limits currently imposed on the use of high strength materials in HPHT applications. (6) This program will also expand the database for environmental cracking in HPHT sour service environments. (7) One of the key deliverables of this effort will be to provide strong technical basis for fugacity-based approaches to material evaluation alongside a superior linkage between laboratory FFP tests and HPHT well environments. (8) Consequently, the project is expected to yield data / model pointing to less constrained process engineering and more cost effective material utilization in the oil and gas industry.

The goal/deliverables of the project are to:

- 1.) Reduce restrictions on use of high strength materials produced by current, simplified methodologies of partial pressure of H₂S that result in over-evaluation of SSC/SCC by laboratory tests versus actual HPHT well environments.
- 2.) Determine the concentration of H₂S species in aqueous solution by Raman spectroscopy

- 3.) Correlate serviceability limits of H₂S partial pressure and pH presently found in NACE MR0175/ISO15156 with more appropriate parameters such as fugacities and activity coefficients that facilitate accurate determination of in-situ pH and soluble H₂S and provide better scalable parameters for defining sour service conditions.
- 4.) Develop SSC/SCC data for commonly used high strength steels and corrosion resistant alloys (CRAs) over a range of HPHT conditions aimed to verify the predicted model trends versus environmental cracking.
- 5.) Develop a broad corrosion database and thermodynamic framework on a software platform.

Overall benefits for ONGC:

Presently ONGC is venturing into HPHT deep sea well conditions of Eastern offshore. The problem that exists today for HPHT wells in terms of corrosion characterization and material selection represents a serious risk for applications requiring higher strength materials. The current approach used in NACE MR0175/ISO15156 (solely based on partial pressure of H₂S and the concept of ideal gases) has the potential for extensive over-conservatism for HPHT material selection for sour service and correspondingly inflated investments and economic consequences. This situation is caused by laboratory evaluation and FFP tests in sour environments at relatively low pressures that have orders of magnitude more soluble H₂S than HPHT well environments and that do not include the concept of H₂S fugacity.

Utilization of more rigorous and accurate thermodynamic modeling based on ensemble Henry's Law and Ionic characterization tools appears to facilitate expanded H₂S limits particularly for high strength materials that can potential expand their field use for HPHT applications. This project is expected to offer ONGC compelling technical basis and data for environmental cracking quantification in sour service environments that include HPHT conditions and providing better linkage between laboratory FFP tests and HPHT well environments.