

The Implications and Practicalities of Adopting the Dissolved H₂S Concentration as the Sour Service Scalable Metric to Improve HPHT Materials Qualification Testing

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ABSTRACT

Gas phase H₂S is synonymous with sulfide stress cracking (SSC) and is routinely used as the 'scalable' parameter to qualify materials for high-pressure, high-temperature (HPHT) wells. Candidate materials for HPHT wells routinely require ANSI/NACE MR0175/ISO 15156 compliance because a few mole ppm of H₂S at high pressure may place the well beyond the 0.05 psia (0.3 kPa) sour service threshold. H₂S partial pressure (P_{H_2S}) has been accepted historically as the scalable sour severity parameter. However, as the total pressure increases, the relationship between P_{H_2S} and the dissolved H₂S concentration becomes non-linear. This limits the robustness of P_{H_2S} as the sour severity metric. Thus, ISO 15156-2:2015/Cir.1:2017 now permits the use of H₂S fugacity (f_{H_2S}), H₂S activity (a_{H_2S}), and H₂S concentration (C_{H_2S}) as alternatives for sour testing. This recent revision is based on evidence that f_{H_2S} and C_{H_2S} each provide better correlations to SCC at elevated total pressures than P_{H_2S} .

This paper will address the merits and challenges of using f_{H_2S} or C_{H_2S} to define sour severity: We will argue that C_{H_2S} is the preferable parameter because it can be measured directly, and it has a direct correlation to hydrogen ingress through the metallurgy that is a precursor to cracking.

Key words: Fugacity, Partial pressure, Sulfide stress cracking (SSC), ANSI/NACE MR0175/ISO15156, H₂S activity, Ensemble Henry's law, HPHT wells, Ionic-equation-of-state (EOS), Non-ideal thermodynamics, material qualification

INTRODUCTION

Candidate materials for high-pressure, high-temperature (HPHT) wells routinely require ANSI[†]/NACE[†] MR0175/ISO[†] 15156¹ (herein referred to as the Standard) compliance⁽¹⁾, because a few mole ppm of H₂S present in the hydrocarbon phase multiplied by the total wellbore pressure is all that is required to place a well beyond the 0.05 psia (0.3 kPa) sour service threshold defined by the Standard. This 0.05 psia threshold of concern applies primarily to material susceptibility to SSC, a low-temperature phenomenon. NACE[†] MR0175, when initially adopted in 1976, addressed SSC only. In subsequent years, the scope of the Standard was expanded to include H₂S-influenced, active path stress corrosion cracking (SCC) at elevated temperatures. However, consideration of these higher temperature phenomena is beyond the scope of this paper, with the supporting literature and discussion restricted to SSC.

Relevant sour service standards still associate H₂S partial pressure (P_{H_2S}) with SSC¹⁻⁴ and this parameter continues to be used to qualify materials for HPHT wells. However, there is recent evidence that SSC susceptibility correlates better with H₂S fugacity (f_{H_2S}) and/or dissolved H₂S concentration in the aqueous phase (C_{H_2S}) at elevated total pressures.⁵⁻⁷ The approval of Ballot 2016-08 led to the recent publication of ISO 15156-2:2015/Cir.1:2017, which permits users the option to define environmental sour severity either by f_{H_2S} , activity (a_{H_2S}), or C_{H_2S} in addition to P_{H_2S} . These alternative sour severity metrics incorporate the thermodynamic non-ideality effects on H₂S partitioning between gas/hydrocarbon and aqueous phases at elevated pressure, temperature, and composition. The challenge now shifts to identifying a quantitative H₂S parameter that is scalable with total pressure from ambient to HPHT conditions. The current best two candidates for HPHT applications are either f_{H_2S} or C_{H_2S} . As both f_{H_2S} and a_{H_2S} are derived from the chemical potential (μ_{H_2S}) and fugacity can be defined in each phase, it is sufficient to consider P_{H_2S} , C_{H_2S} , and f_{H_2S} only.⁸

While it is widely accepted that defining sour service limits based on P_{H_2S} is problematic, there is no universal acceptance of an alternative metric. There has been significant progress in understanding the thermodynamics of H₂S under HPHT conditions,^{5, 9-12} but there are only a handful of studies linking this non-ideal thermodynamic behavior to actual SSC outcomes.^{9, 10} Lastly, proper risk-benefit analyses of adopting an alternative modern H₂S-SSC correlation metric are scarce.¹³

The critical issue is therefore to determine which parameter, f_{H_2S} or C_{H_2S} , best characterizes higher pressure sour systems for material qualification purposes. On the one hand, several authors⁵⁻⁷ discuss differences in H₂S solubility in high pressure versus low pressure systems and the relationship between concentration, fugacity, and activity. No evidence of the controlling SSC mechanism was provided. On the other hand, Krishnamurthy *et al.*⁷ recognized the impact of C_{H_2S} -pH on the “mechanistic” control of SSC with respect to existing evidence and empirical modeling, but is not a mechanistic assessment that proves the role of C_{H_2S} in SSC. Regardless, once the industry arrives at a consensus on the preferred sour severity metric, and a precise quantification of the parameter is demonstrated, its significance to SSC testing outcomes with similar accuracy will need to be established.

In an effort to further the discussion, this paper addresses the merits and challenges of the two modern approaches to defining sour severity: f_{H_2S} ⁽²⁾, and C_{H_2S} ⁽³⁾. Focusing on C_{H_2S} is preferable as it has a direct correlation to hydrogen ingress through the metallurgy that is a precursor to cracking. The following

[†] Trademark.

(1) The ramifications for categorizing a well as sour are profound, because while the Standard¹ is not a regulatory document *per se*, it has been incorporated by reference in its entirety by many regulatory agencies worldwide, and for many jurisdictions its technical definitions and requirements carry the compulsion of a regulatory writ.

(2) The computationally-based species activity value derived from experimental data. Specific to the gas and non-aqueous phase.

(3) The measured concentration of molecular H₂S in the aqueous phase.

literature review is intended to provide clarity on this important subject and provide a logical path forward to improving material qualification testing for HPHT sour service conditions.

The Dilemma of Relying on P_{H_2S} for HPHT Sour Service Testing

Performing actual NACE-compliant H_2S fitness for service qualification tests at full wellbore pressure is not practical for most projects. Sour service autoclaves that can safely maintain a pressure differential of $> 10,000$ psig for 720 hours are rare, costly, and have limited internal volumes. Therefore, to reduce costs and to avoid the complexities, the Standard permits sour service testing in *low pressure laboratory equipment* provided that the candidate material is qualified in a suitable environment that is *at least as severe as the field environment*.¹ This is generally accomplished by using a “test gas containing H_2S and CO_2 at the same partial pressures at the intended service.”¹ This approach ignores the influence of high pressure on the cracking behavior of susceptible alloys. The consequence of this policy, while not fully understood at the time of adoption in 1976, results in a conservative, or possibly under-conservative, design philosophy.¹³ The intrinsic over-conservatism of the above NACE policy becomes consequential when selecting materials for mildly sour HPHT wells with wellbore pressures $> 10,000$ psig.^{5, 6, 14} (The policies leading to over/under-conservative design will be addressed in the following paragraphs.)

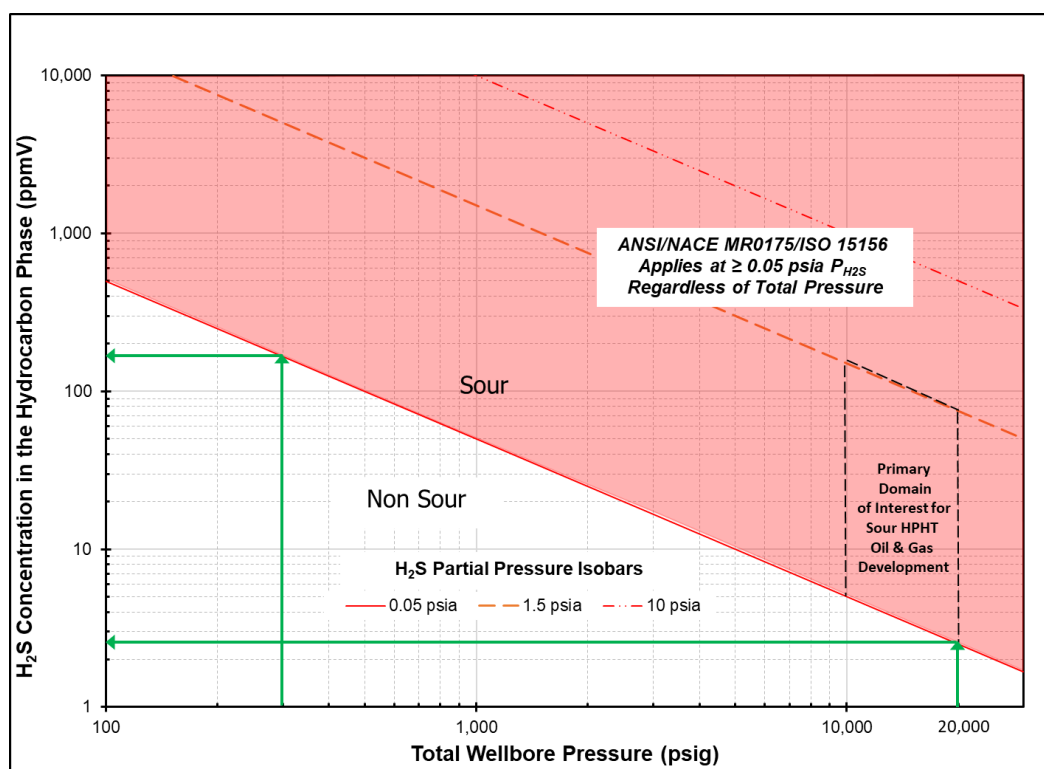


Figure 1. Minimum y_{H_2S} needed to meet or exceed the 0.05 psia H_2S criteria defined by the Standard.¹

Table 1. Minimum y_{H_2S} needed to maintain the 0.05 psia H_2S criteria at multiple P_T .

Total Pressure (psig)	0	300	20,000
y_{H_2S} (mole ppm)	3400	160	2.5

The minimum H₂S concentration in the *gas/hydrocarbon phase* ($y_{\text{H}_2\text{S}}$) required to reach 0.05 psia H₂S is shown in Figure 1 and Table 1. For a mature well with a total pressure (P_T) of 300 psig (low pressure), $y_{\text{H}_2\text{S}}=160$ ppm is required to exceed 0.05 psia H₂S threshold. In contrast, for a 20,000 psig well, $y_{\text{H}_2\text{S}}=2.5$ ppm is *merely* needed to trigger regulations.⁴ Therefore, when comparing 300 psig versus 20,000 psig, the minimum $y_{\text{H}_2\text{S}}$ needed to reach the sour severity threshold is reduced by 64 times. A universal H₂S sour service threshold based on its $P_{\text{H}_2\text{S}}$ ($y_{\text{H}_2\text{S}} \times P_T$) implies that the total pressure drives the SSC mechanism.

The issue is confounded further because materials may be qualified for sour service at 14.7 psia with “H₂S at the partial pressure of [the] intended service.”¹ Performing laboratory tests at atmospheric pressure, while maintaining the field $P_{\text{H}_2\text{S}}$, requires increasing $y_{\text{H}_2\text{S}}$. For example, a 20,000 psig HPHT well containing $y_{\text{H}_2\text{S}}=2.5$ mole ppm yields a pseudo- $P_{\text{H}_2\text{S}}$ of 0.05 psia.¹⁵ At atmospheric pressure, to maintain the 0.05 psia $P_{\text{H}_2\text{S}}$ the test gas must contain $y_{\text{H}_2\text{S}}=3400$ mole ppm (see Table 1). If the solubility of H₂S remained constant with total pressure (i.e., the gas solubility is linear with pressure) then substituting total pressure with a higher $y_{\text{H}_2\text{S}}$ in the test gas would be inconsequential. This not the case. H₂S solubility decreases with increasing total pressure by at least an order of magnitude (refer to Figure 13). Thus, qualifying materials based on equivalent $P_{\text{H}_2\text{S}}$ may lead to over-conservatism particularly when qualifying materials for service conditions with total pressures > 10,000 psig (69 MPa).^{5-7, 12}

In addition to over-conservative design concerns, the Standard also allows for a simplification for systems whose total pressure exceeds the bubble point/saturation pressure (e.g. “gas-free wells”). The assumption is made that the severity of the environment at pressures above the bubble point can be characterized by the $P_{\text{H}_2\text{S}}$ calculated at the bubble point, which may be non-conservative when considering the modern $f_{\text{H}_2\text{S}}$ and $C_{\text{H}_2\text{S}}$ approaches.⁸

Clearly, $P_{\text{H}_2\text{S}}$ is not an *appropriate* metric for HPHT material selection and design, because it is not scalable. Defining material sour service limits strictly on the basis of $P_{\text{H}_2\text{S}}$ implies that the effect of total pressure on cracking susceptibility is inconsequential. The premise that material qualification laboratory tests, conducted at atmospheric pressure, can be designed merely by decreasing the total pressure and increasing the $y_{\text{H}_2\text{S}}$ to maintain the *same* $P_{\text{H}_2\text{S}}$ expected in the field and yield an *identical* SSC outcome for the same oilfield material is flawed. High-pressure laboratory tests and field experience confirm that the risk of cracking is significantly lower than would be expected based laboratory tests results performed at atmospheric pressure with the same $P_{\text{H}_2\text{S}}$.¹⁶ Therefore, resolution on the feasibility of implementing either $f_{\text{H}_2\text{S}}$ or $C_{\text{H}_2\text{S}}$ is an important contribution to improving material qualification testing for HPHT wells, although is not the sole consideration for users.

Nevertheless, the industry needs to adopt a new realistic design metric that is fully scalable between atmospheric pressure and 20,000 psig. The authors argue that $P_{\text{H}_2\text{S}}$ should be replaced with $C_{\text{H}_2\text{S}}$ as the new sour service metric.⁽⁴⁾ Preference for $C_{\text{H}_2\text{S}}$ does not preclude the option to select $f_{\text{H}_2\text{S}}$ or $a_{\text{H}_2\text{S}}$ as an alternative sour severity metric, pursuant that the thermodynamic calculations are performed correctly, if so desired. The following sections provide the history and rationale for adopting $C_{\text{H}_2\text{S}}$ as the sour severity metric.

The Theory and Evolution of the Modern H₂S-SSC Correlation Metrics

Historical Approach to Mitigating SSC—Ideal Gas Behavior

⁽⁴⁾ Selecting materials based on a conservative design criterion is critical to ensure safety. However, there is a distinction between adopting a mechanistically consistent, fully-scalable sour service metric, and applying an appropriate margin of safety to account for system uncertainty.

SSC is a cathodically-controlled, corrosion-based failure mechanism driven by atomic hydrogen, produced from sulfide-induced corrosion, penetrating the metal surface (Figure 2). SSC usually occurs at low to moderate temperatures (< 150 °F). The major environmental parameters influencing SSC susceptibility are the *in-situ* pH, chloride concentration, and dissolved H₂S. From a cracking mechanism perspective, it is either C_{H2S}^{5, 17} or the *f*_{H2S}^{9, 10, 18} that influences SSC at the crack tip, rather than the P_{H2S}. For convenience, however, the Standard categorizes SSC susceptibility based on P_{H2S} as a surrogate for the C_{H2S}.

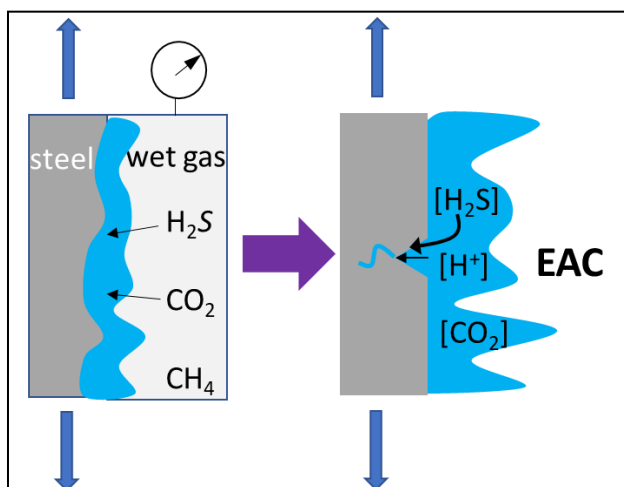


Figure 2. Simplified illustration of the SSC mechanism. SSC requires an aqueous phase in contact with the metal surface.

The Standard partial pressure thresholds *implicitly* presume that the P_{H2S} is proportional to C_{H2S} via the Strict Henry's Law, which assumes ideal gas behavior:

$$C_{H_2S} = (k_{H_2S})_{ideal} \cdot (y_{H_2S} \cdot P_T) \quad 1$$

where $(k_{H_2S})_{ideal} = 230 \text{ mg/L/psia}$ (0.1 mol/L/atm) for freshwater at 75 °F and 14.7 psia¹⁹⁻²¹. (Refer to "Glossary of Thermodynamic Terms" for all other symbols.) P_{H2S} is a relatively accurate approximation for C_{H2S} at room temperature and low total pressures for dilute solutions. Irrespective of the total pressure of the system, however, the sour service limits for alloys specified in the Standard are defined in terms of the partial pressures of H₂S and CO₂. The Standard assumes that the ideal gas behavior governs and that the influence of the hydrocarbon phase on the cracking susceptibility is negligible and can be ignored.

Figure 3 illustrates the regions of environmental severity with respect to SSC as a function of the *in-situ* pH of the *aqueous phase* and the P_{H2S} of the *hydrocarbon phase* according to the Standard.¹ The pH-P_{H2S} relationship was intended originally for carbon and low-alloy steels with hardness values ≤ 22 HRC. It has also been applied by various users to visualize/design material qualification tests and establish susceptibility to SSC boundaries for high strength steels and alloys.²² The regions of environmental severity assume ideal gas law behavior, because the authors designed the diagram to reflect the behavior expected for oil and gas wells whose total operating pressures were ≤ 250 psig.^{3, 7, 23, 24}

The underlying assumptions leading to over-conservatism has been to extrapolate the strict Henry's Law to non-ideal conditions at high pressure, assuming P_{H2S} remains directly proportional to C_{H2S}. In reality, the relationship between C_{H2S} and P_{H2S} is non-linear within the HPHT domain^{25, 26} (see Figure 4). The flatline behavior, illustrated by the solid purple line in Figure 4, is a result of exceeding the bubble point pressure and reflects the limited solubility of H₂S in brine.²⁵⁻²⁷

The historical practice of extrapolating the strict Henry's Law to the full wellbore total pressure was suitable and afforded reasonable safety factors for *low-total pressure* systems. As HPHT wells have become more prevalent and the total pressures continue to rise, the safety margins have increased significantly to the point that they are onerous and impractical. While a sour service limit of 0.05 psia H₂S may be appropriate for wells with low total pressures, the authors are not aware of any evidence demonstrating that 0.05 psia (0.3 kPa) H₂S ought to be the sour service limit between 10,000 psig (69 MPa) and 20,000 psig (138 MPa) at 75 °F (24 °C).

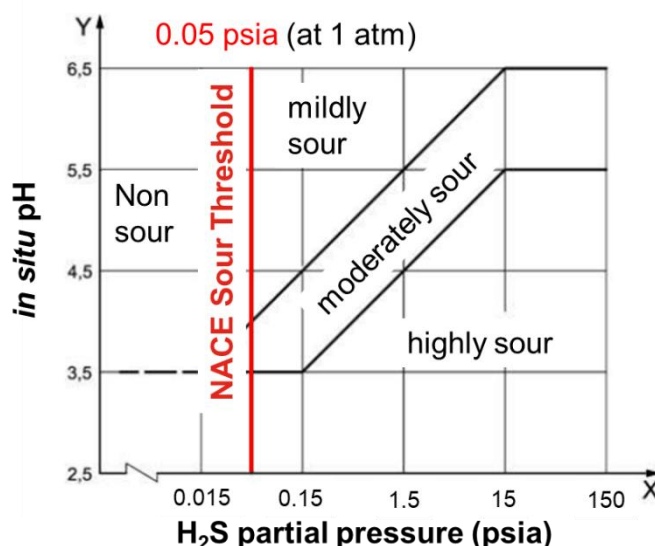


Figure 3. Regions of environmental severity with respect to the SSC of carbon and low alloy steels. The plot was modified to emphasize the sour service limit of 0.05 psia (0.3 kPa).¹

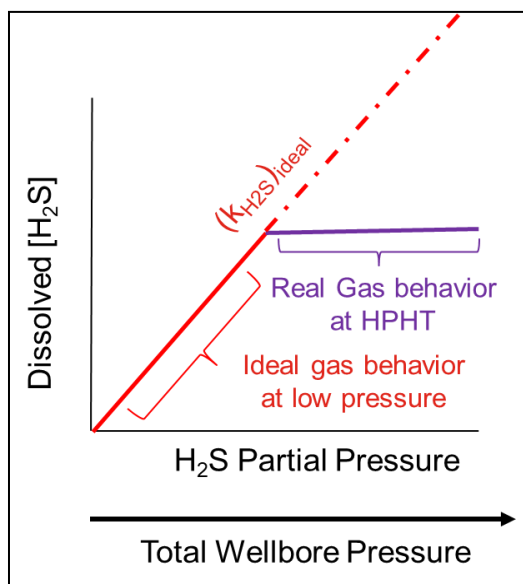


Figure 4. Simplified illustration of the ideal and real phase behavior between C_{H_2S} and the P_{H_2S} for a constant y_{H_2S} as a function of total pressure.

Recent Changes to ANSI/NACE MR0175/ISO 15156

Recognizing the limited relevancy of the historical “regions of environmental severity” to modern HPHT applications, various agencies involved in maintenance of the Standard have agreed to the recent

publication of ISO 15156-2:2015/Cir.1:2017 which permits users the option of implementing P_{H_2S} , f_{H_2S} , a_{H_2S} , or C_{H_2S} as metrics to define environmental severity. For clarity, Table 2 categorizes the modern sour service metrics based on phase behavior and whether the parameter is directly measurable in the lab or is derived from rigorous computational modeling. While the adoption of ISO 15156-2:2015/Cir.1:2017 is an important contribution and milestone, the standard *does not* provide clear guidance on the validity of, or how to validate, the alternative sour severity metrics.

Table 2. Sour severity metrics recognized by the Standard.¹ Refer to “Glossary of Thermodynamic Terms” for symbol definitions.

Phase	Direct Approach: Physical	Indirect Approach: Theoretical	Convergence
Hydrocarbon (Gas or Liquid)	Partial Pressure: ¹ $P_{H_2S} = y_{H_2S} \cdot P_T$	Fugacity: ⁸⁻¹⁰ chemically equivalent P_{H_2S} $f_{H_2S} = \phi_{H_2S} \cdot y_{H_2S} \cdot P_T$	As $P_T \rightarrow 1 \text{ atm}$, $\phi_{H_2S} \rightarrow 1$ $f_{H_2S} = P_{H_2S}$
Aqueous (Liquid Only)	Concentration: ^{5, 6} $C_{H_2S} = k_{H_2S} \cdot P_{H_2S}$	Activity: ²⁸ effective concentration $a_{H_2S} = \gamma_{H_2S} \cdot C_{H_2S}$	As $x_{NaCl} \rightarrow 0$, $\gamma_{H_2S} \rightarrow 1$ $a_{H_2S} = C_{H_2S}$
Can the parameter be directly measured in the lab?	Yes	No	

P_{H_2S} remains the *de facto* metric to define sour severity for a variety of reasons including: Historical experience, safety concerns, limited available data, and/or logistical issues with capturing and preserving field samples. To safely reduce over-conservatism for material qualification in mildly sour environments at HPHT conditions, the industry needs a universally accepted P_{H_2S} alternative that is empirically-based and is fully scalable across the entire service domain. Of the metrics recognized by the Standard, a concentration-based metric is the only metric that is directly experimentally-verifiable, appropriate for all water to gas (WGR) volumetric ratios, and could be used to translate historical SSC material testing experience (generally obtained at total pressures < 5000 psig [34.6 MPa]) to predict SSC behavior between 10,000 and 20,000 psig (69 to 138 MPa) – the high-pressure domain of interest.

Having demonstrated the limitations of using P_{H_2S} to predict H_2S behavior at elevated pressures, the following sections provide a review of industry’s attempt at implementing alternative modern approaches to better correlate the non-ideal behavior of H_2S within the HPHT domain to actual experimental data.

Modern Approach to Mitigating SSC—Non-Ideal Gas Behavior

In 2005, Nelson and Reddy compared the C_{H_2S} values predicted from the strict Henry’s Law, the Fugacity-Corrected Henry’s Law, and the Ensemble Henry’s Law equations.¹² As shown in Figure 5, the Ensemble Henry’s Law provided the best correlation to the experimentally-determined C_{H_2S} values. These observations were later confirmed by Kumar *et al.* in 2013²⁹ at C_{H_2S} relevant for mildly sour wells. The most intriguing aspect is the C_{H_2S} remains constant between ~1800 psia and 10,000 psia total pressure. This phenomenon has been observed by others.^{25-27, 30, 31}

The observed dissolved H_2S “saturation plateau” arises from the fact that H_2S does not partition equally between the hydrocarbon and aqueous phases since H_2S has limited solubility in water. Therefore, for a given y_{H_2S} , C_{H_2S} increases with increasing total pressure until a “saturation plateau” is reached. Within this “saturation plateau” region, the C_{H_2S} is nearly independent of total pressure.¹⁰

Nelson and Reddy applied the Ensemble Henry’s Law approach to compare the phase behavior of a well at 10,000 psi (69 MPa) total pressure containing 1 mol% H_2S (100 psia [690 kPa] H_2S) and a low-pressure