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## EFFECT OF HYDROGEN ON STEELS IN HYDROGEN SULFIDE-CONTAINING AND OTHER ENVIRONMENTS AT GAS FACILITIES

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**Abstract.** The impact of hydrogen sulfide raw materials on steel equipment and pipelines is known and is associated not only with internal corrosion processes, but also with the hydrogenation of carbon and low-alloy steels used. Penetration of hydrogen into steel can lead to the loss of its strength properties and subsequent destruction of gas pipelines operated under high pressure conditions. The manifestations of cracking characteristic of hydrogen sulfide environments, which are a consequence of the penetration of hydrogen into steel, are the most dangerous from the point of view of the safety and reliability of the operation of facilities for the production and transportation of corrosive gas. The effect of  $H_2S$  on the decrease in ductility of the main types of structural steels was studied based on the results of simulation tests. The formation of blisters (bloatings) and cracks on the surface of steels due to the effect of hydrogen on steel was recorded. The study of the phase composition and properties of corrosion products was carried out in order to assess their possible influence on the processes of steel hydrogenation. The formation of evenly distributed on the surface and the densest corrosion deposits will hinder both the corrosion processes and the penetration of hydrogen into steel. A decrease in the plastic properties of steel is also observed when exposed to hydrogen, which can be transported both separately and together with methane through the main gas pipelines. The main possible means of protecting steels that are unstable to hydrogenation is the use of corrosion inhibitors. It was established that the most effective corrosion inhibitors with rational technologies of application and dosage can protect steels from penetration of hydrogen into them and their destructive effect.

**Keywords:** gas pipeline, steel microstructure, blistering, hydrogenation, steel cracking, corrosion products, corrosion inhibitor

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## ИССЛЕДОВАНИЕ ВЛИЯНИЯ ВОДОРОДА НА СТАЛИ В СЕРОВОДОРОДСОДЕРЖАЩИХ И ДРУГИХ СРЕДАХ НА ГАЗОВЫХ ОБЪЕКТАХ

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**Аннотация.** Воздействие сероводородного сырья на стальное оборудование и трубопроводы известно и связано не только с процессами внутренней коррозии, но и с наводороживанием применяемых углеродистых и низколегированных сталей. Проникновение водорода в сталь может приводить к потере ее прочностных свойств и последующему разрушению газопроводов, эксплуатируемых в условиях повышенных давлений. Характерные для сероводородных сред проявления растрескивания, являющиеся последствием проникновения водорода в сталь, наиболее опасны с точки зрения безопасности и надежности работы объектов по добыче и транспортировке коррозионно-агрессивного газа. Исследовано воздействие  $H_2S$  на снижение пластичности основных видов конструкционных сталей по результатам имитационных испытаний. Зафиксировано образование блистерингов (вздутий) и трещин на поверхности сталей вследствие воздействия водорода на сталь. Проведено изучение фазового состава и свойств продуктов коррозии с целью оценки их возможного влияния на процессы наводороживания стали. Образование равномерно расположенных по поверхности и наиболее плотных коррозионных отложений будет затруднять процессы коррозии и проникновение водорода в сталь. Снижение пластических свойств стали наблюдается и при воздействии водорода, который может транспортироваться как в отдельности, так и совместно с метаном по магистральным газопроводам. Основным возможным средством защиты сталей, нестойких к наводороживанию, является применение ингибиторов коррозии. Установлено, что наиболее эффективные ингибиторы коррозии с рациональными технологиями применения и дозировкой могут обеспечить защиту сталей от проникновения в них водорода и его разрушительного действия.

**Ключевые слова:** газопровод, микроструктура стали, блистеринг, наводороживание, растрескивание стали, продукты коррозии, ингибитор коррозии

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## INTRODUCTION

The reliable and secure functioning of infrastructure is essential for the effective exploitation of oil and gas reserves. Corrosive components like carbon dioxide ( $\text{CO}_2$ ) and hydrogen sulfide ( $\text{H}_2\text{S}$ ), especially when water is present (either formation water or from condensation), can lead to widespread or localized corrosion and fractures [1].

Environments containing  $\text{H}_2\text{S}$  are notably aggressive, leading to the hydrogenation of steel and causing both localized and general hydrogen sulfide corrosion (HSC) [2]. The permeation of hydrogen into steel poses a heightened risk, and thus the durability of steel structures and pipelines in high  $\text{H}_2\text{S}$  environments is evaluated with consideration of the potential for hydrogen induced cracking [3].

It is important to recognize that the operational conditions at oil and gas facilities vary depending on whether the primary extracted fluids are oil or gas/gas condensate. These differences affect the types of corrosion that occur within pipelines. Previous research [4] has indicated that a particularly hazardous form of internal corrosion in gas pipelines involves localized corrosion at the top of the pipe where moisture condenses, collects, and then flows along the lower external curve of the pipe.

The Orenburg and Astrakhan gas condensate fields are examples where conditions conducive to HSC complications are present [2]. These sites are not unique in their susceptibility to HSC and hydrogenation issues. Moreover, pipeline systems for the reinjection of “sour gases” (a mixture of  $\text{H}_2\text{S}$  and  $\text{CO}_2$  extracted from fluids during processing) are being developed at the Astrakhan field for disposal and enhanced condensate recovery in later production stages [5]. The  $\text{H}_2\text{S}$  concentration in the gases transported through these pipelines will be considerably higher than in the initial extraction.

There is also growing interest in hydrogen as a fuel and its combined transportation with natural gas through main pipelines, as well as in the storage of hydrogen in underground facilities [6 – 7]. The use of hydrogen raises inevitable concerns regarding its explosive nature and its effect on the mechanical integrity of pipelines made from carbon/low alloy steel.

Some studies [8] suggest that hydrogen-containing gases could impact steel in a manner similar to  $\text{H}_2\text{S}$ : atomic hydrogen is generated, diffuses into the steel from the surface, and then dissociates, causing local dis-

integration of the metal’s crystal lattice. This can lead to the development of hydrogen-induced microcracks, which, under the high pressure of the gas pipeline and continued hydrogen exposure, may result in hydrogen cracking. As mentioned in [9], storing hydrogen in underground gas storage (UGS) facilities, along with natural gas, might induce a variety of effects, including steel hydrogenation, thereby intensifying the internal corrosion of steel structures and pipelines. The potential effects of hydrogen on steel during transportation and storage are not thoroughly understood and are vital subjects for future research.

Therefore, it is imperative to explore the trends, progression, and mechanisms of corrosion damage, along with the protective strategies employed at gas processing facilities to counteract HSC and steel hydrogenation. The corrosive effects of  $\text{H}_2\text{S}$  and hydrogen ions, generated during the cathodic process, impact steel not only in the liquid phase but also in the vapor phase. This dual-phase impact requires careful consideration when evaluating the corrosive risks of an environment and choosing appropriate protective measures.

## MATERIALS AND METHODS

The following types of carbon and low-alloy steels were selected for testing: 09G2S, St20, S–75, X42SS, and 30KhMA. These steels are commonly utilized in different components and segments of wellhead equipment and pipeline systems within gas field operations.

To assess their performance under HSC conditions and to collect corrosion products for subsequent analysis, tests were carried out in controlled environments using autoclaves. These simulated conditions mimicked the effects of mineral content in the environment and the partial pressures ( $P$ , MPa) of  $\text{CO}_2$  and/or  $\text{H}_2\text{S}$ , allowing for the replication of the corrosion rates observed in actual field conditions. The autoclave tests were conducted for 120 h at temperatures ( $T$ ) of 30 or 90 °C. Aqueous environment with mineralization level of 100 (MB1) and 200 g/l (MB2), with the addition of 0.25 g/l of  $\text{CH}_3\text{COOH}$ , were used. A 0.5 % NaCl solution was used for the tests in the presence of hydrogen. The total corrosion rate ( $K$ , mm/yr) was determined based on the weight loss of the samples from the test results. The effect of hydrogenation was evaluated by the steel’s ability to retain plasticity before and after exposure to the corrosive environment, measured by the number of kinks in wire samples (SV08A steel) before destruction accor-

ding to GOST 1579 – 93 [10]. The decrease in plasticity ( $Pl$ , %) was determined by the number of steel wire kinks after autoclave tests compared to the initial value.

Metallographic analysis of the steels included determining the microstructure according to GOST 8233 [11]. A Zeiss Axio.Vert A1 inverted metallurgical microscope with the Thixomet image analyzer was used for metallographic studies at magnifications of 100 – 1000 times.

The technique for analyzing the phase composition of corrosion products by  $X$ -ray diffraction (XRD) method, based on registering the dependence of  $X$ -ray reflection intensity (reflections) by the crystal lattices of compounds on the diffraction angle, was described earlier in paper [2], with subsequent interpretation of the diffraction pattern.

## RESULTS AND DISCUSSION

The microstructure of steels significantly influences in the development of corrosion defects and hydrogen permeation into the metal in scenarios involving HSC. According to [12], the highest amount of hydrogen diffuses into the sample of heat-treated carbon steel API X65, a commonly used foreign pipe steel grades, that exhibits a microstructure with an increased proportion of pearlite and a reduced amount of ferrite, akin to the types studied by the authors. This specific microstructural composition leads to diminished steel strength and plasticity. Notably, within the pearlite phase – characterized by its lamellar structure of alternating cementite and ferrite – gaps between the lamellae act as channels that facilitate the diffusion and accumulation of hydrogen. The occurrence of microcracking as a result of hydrogen sulfide embrittlement within the steel's crystalline structure may limit further permeation of hydrogen into steel. This phenomenon could partly account for the non-uniform distribution of hydrogen across the steel's thickness, with the highest concentrations typically found in the surface layer. The presence of corrosion-active non-metallic inclusions (CANMIs) in the steel can also contribute to the deterioration of steel strength properties in instances of internal corrosion. Manganese compounds such as  $MnS$ , often found in combination with aluminum inclusions in steel, serve as notable examples of CANMIs that function as hydrogen “traps” [13]. The interface between these inclusions and the steel matrix acts as a repository for hydrogen atoms, providing a locale for these atoms to recombine into molecular  $H_2$ .

This interaction highlights a critical mechanism through which the microstructure of steel, influenced by the presence of such inclusions, can impact the overall resilience and integrity of the material in corrosive environments, particularly those encountered in gas fields (Figure).

The microstructure of the samples is as follows:

- S75 steel exhibits finely dispersed secondary sorbite that has retained martensitic orientation;
- X42SS is a ferritic-perlitic steel;
- St20 is a ferritic-perlitic steel with non-uniform distribution of lamellar pearlite;
- 30KhMA is a coarse-grained ferritic-perlitic steel where ferrite forms a network at the boundaries of primary austenitic grains, and ferrite needles grow from the ferrite network into perlite;
- 09G2S is a fine-grained ferritic-perlitic steel.

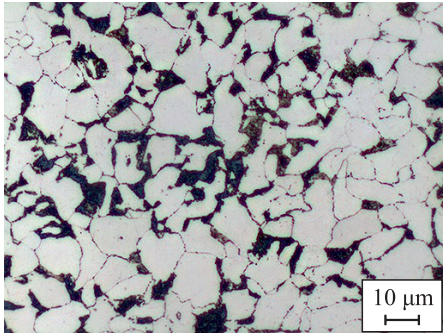

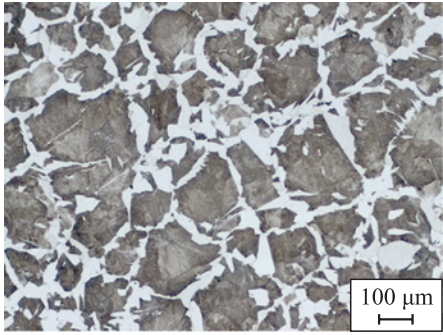

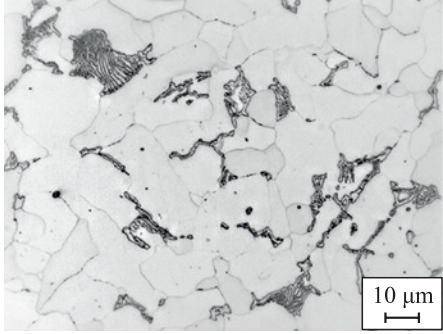

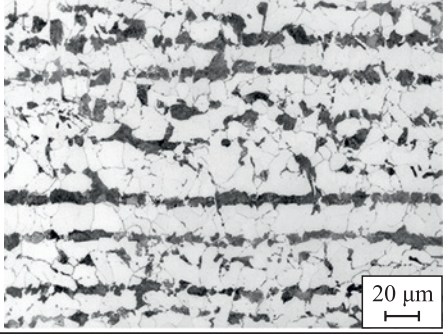

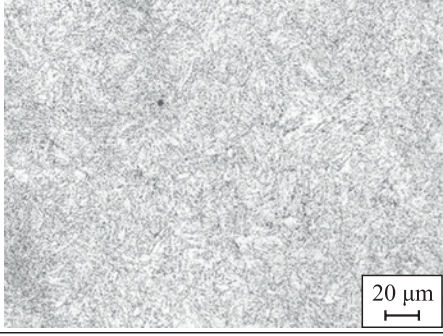
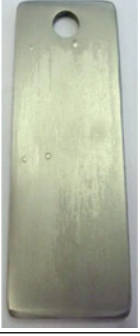
Hydrogen permeation has visibly altered the appearance of the steel samples, as evidenced by the formation of blisters of varying sizes on the surface of most steels under examination, with 09G2S steel presenting the smallest blisters. The surface of the 30KhMA steel is extensively marked with small cracks, and sporadic blistering is also evident. These blisters, when subjected to critical hydrogen pressure levels, rupture and lead to crack formation.

The inherent stresses in the steel's crystal structure, along with the pre-existing microstructural characteristics, are implicated in the initiation and expansion of microcracks [14]. According to the findings in [15], the occurrence of blisters on 13KhFA and 05KhGB steels is related to the presence of complex corrosion-active non-metallic inclusions within the metal, which also predispose these steels to cracking.

Subsequent tests were conducted on St20 steel, which exhibited the highest blister count [2], and 09G2S steel, which is predominantly used in gas infrastructure. Both St20 and 09G2S steels possess a ferritic-perlitic microstructure with a non-uniform distribution of these phases, contributing to their heterogeneous nature. This heterogeneity compromises their resistance to both corrosion and hydrogenation.

Table 1 reveals that the  $K$  value of the samples made from St20 and 09G2S steels after the tests in and above the MB2 aqueous solution ranges from 0.319 to 0.569 mm/yr (for the aqueous phase) and from 0.156 to 0.227 mm/yr (for the vapor phase). In a different MB1 environment, the  $K$  value is higher: 0.8 and 0.52 – 0.55 mm/yr in and above the aqueous electrolyte, respectively. The probable reason is that solubility of corrosive  $H_2S$  in the higher mineralized MB2 solution is limited. High mineralization can result in lower evaporation and condensation of such water required for HSC to propagate on the samples in the vapor phase. However, despite this, localized corrosion defects are observed on the steel surface of the sample tested above the MB1 solution (Table 2). Tests conducted by the authors under the conditions of forced moisture condensation on carbon steels with  $H_2S$  purging showed [16] that in the humidified



Steel	Microstructure	Appearance
09G2S		
30KhMA		
St20		
X42SS		
S75		

Microstructure and appearance of various structural steels after simulation tests in the MB2 environment at  $P_{\text{CO}_2} = 0.13 \text{ MPa}$  and  $P_{\text{H}_2\text{S}} = 0.54 \text{ MPa}$

Микроструктура и внешний вид различных конструкционных сталей после имитационных испытаний в среде MB2 при  $P_{\text{CO}_2} = 0,13 \text{ МПа}$  и  $P_{\text{H}_2\text{S}} = 0,54 \text{ МПа}$

Table 1. Conditions and results of simulation tests in H<sub>2</sub>S-containing environmentsТаблица 1. Условия и результаты имитационных испытаний в H<sub>2</sub>S-содержащих средах

Number of the test conditions	Steel	Phase	$P$ , MPa		$T$ , °C	$K$ , mm/yr	$Pl$ , %
			H <sub>2</sub> S	CO <sub>2</sub>			
MB2 solution							
1	St20	Aqueous	0.54	0.13	30	0.458	71
2	09G2S	Aqueous	0.54	0.13	30	0.465	
3	St20	Vapor	0.54	0.13	30	0.156	35
4	St20	Aqueous	0.60	–	30	0.319	60
5	St20	Vapor	0.60	–	30	0.227	57
6	09G2S	Aqueous	0.13	0.54	30	0.569	–
7	09G2S	Aqueous	0.60	0.54	30	0.525	60
8	St20	Aqueous	0.60	0.54	30	0.454	
MB1 solution							
9	St20	Aqueous	1.50	0.80	30	0.797	74
10	St20	Vapor	1.50	0.80	30	0.817	66
11	St20	Aqueous	1.50	0.80	90	0.529	40
12	St20	Vapor	1.50	0.80	90	0.557	32

vapor phase, the local *K* value, calculated by the depth of pittings formed, reached 1.232 – 1.366 mm/yr.

The microstructural characteristics of steel, particularly the inclusion of CANMIs such as manganese sulfides, are pivotal in the development of pitting lesions in HSC scenarios [17]. These CANMIs, due to their dissimilarity with the steel matrix, act as precursors for the formation of localized corrosion defects. This typically occurs either through the dissolution of the CANMIs themselves or the steel immediately surrounding them. One of the primary reasons behind the corrosive influence of CANMIs is their heterogeneity, which induces elevated stress levels in the adjacent steel matrix. This stress is a result of the mismatched thermal expansion coefficients between the CANMIs and the steel matrix during the steel's production, which involves cycles of heating and subsequent cooling [18]. After the steel cools the region with increased tensile stresses may form around the CANMIs, accelerating internal corrosion.

The effect of steel hydrogenation was evaluated by the reduction of its plastic properties, subsequently resulting in hydrogen embrittlement, and deterioration of metal strength characteristics. As shown in Table 1, the *PI* value after tests at 30 °C in both environments with H<sub>2</sub>S ranges from 60 to 74 % for the aqueous phase and from 35 to 66 % for the vapor phase. Traces of blistering are observed on the surface of the samples after exposure to the aggressive environment (Table 2). It should be noted that in both phases for the MB2 environment, when the test temperature is increased to 90 °C, the *K* value decreases by 33 %, and *PI* drops by 45 to 50 % (Table 1).

Hydrogenation may slightly decrease as the temperature rises due to higher rates of conjugated electrochemical reactions: the cathodic process of hydrogen atom molization on the steel surface is intensified, reducing their ability to permeate inside the metal, as observed by the authors [19]. Another reason why hydrogen permeation and HSC are limited may be the fact that at elevated temperatures, densely packed and evenly distributed corrosion products form faster, acting as a barrier that creates obstacles preventing corrosion components from permeating to the steel surface.

The assessment of the samples' appearance after simulation tests and XRD analysis revealed (Table 2) that corrosion products in the vapor and water phases have different thicknesses and phase compositions. Precipitations in the vapor phase form when the water film is thin. It is suggested that in the vapor phase, only 40 % of the compounds of the corrosion products have a crystalline structure. The majority of them (60 %) did not have enough time to form and remained as looser and unconsolidated X-ray amorphous compounds. In the aqueous phase, the sediment film completely crystallized, becoming thicker and denser.

The results of XRD analysis (Table 2) indicate that in both phases, the main corrosion product is iron sulfide, represented by its two crystal forms: tetragonal FeS (mackinawite) and cubic FeS. The presence of cubic FeS distinguishes these results from the previously obtained data [2]. The results presented in this paper show significant differences, as CH<sub>3</sub>COOH was added to the aqueous environments. Such acidification of the environment

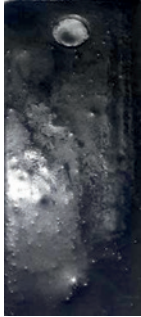



alters the composition of corrosion products and leads to the formation of cubic FeS in addition to the tetragonal form. As a volatile compound,  $\text{CH}_3\text{COOH}$  evaporates along with  $\text{H}_2\text{S}$  and contributes to steel fracture in the vapor phase. Additionally, in this phase, cubic FeS precipitates are also formed (Table 2). The formation of deposits with different crystal structures and different faces of FeS will make the film less cohesive and monolithic, thus reducing its barrier (protective) functionality.

The XRD method is based on the phenomenon of  $X$ -ray diffraction on a three-dimensional crystal lattice. In this case,  $X$ -rays scattering by crystals correlates with the arrangement of atoms in the crystal. Therefore, each crystalline substance is characterized by a set of peaks in the diffraction pattern, where the position of their reflections is constant, and the relative intensity depends on the substance's content in the mixture. The main factors causing changes in the width of the reflections are the structural features of phases (such as the size of crystallites – coherent scattering region (CSR)) or the structural features of the crystal lattice. The EXD data

facilitates the determination of the crystallite size distribution (CSD) within a polycrystal or identifies the minimum particle size maintaining an accurate crystal structure. The methodology for calculating the CSD relies on the analysis and application of the broadening of diffraction lines, represented by  $\beta$ , employing the Selyakov-Scherrer equation [20]. This technique underpins the evaluation of the CSD for FeS (T) compound particles. As illustrated in Table 2, the experimentally measured  $\beta$  values for the samples (post-exposure to aqueous and vapor phases) exhibit variations of different magnitudes from the standard value ( $\beta = 0.1697^\circ$ ), which is typical for the 001 peak position of mackinawite. These discrepancies suggest the occurrence of lattice defects (such as microstresses, isomorphism, etc.) in the samples. Additionally, it was observed that mackinawite crystals formed in the aqueous phase have a significantly larger CSD, up to eight times that of corrosion products formed in the vapor phase. As a result, the FeS film produced in the vapor phase is thinner and possesses inferior protective qualities compared to its aqueous phase counterpart. The findings imply that crystal growth is more rapid

**Table 2. Characteristics of the precipitate and crystal structure of the obtained compounds of mackinawite and appearance of steel (St20) samples for various test conditions (numbering of the experimental conditions is given in Table 1)**

**Таблица 2. Характеристика осадка и кристаллической структуры полученных соединений макинавита и внешний вид стальных (Ст20) образцов (нумерация приведена по табл. 1)**

Number of the test conditions	Ratio		$\beta$ (for $hkl^{***}$ -peak FeS (T) – 001), deg	CSR, nm	With corrosion products	Without corrosion products
	phases, Cr/X*	of crystalline compounds**				
1	100/0	95 % FeS (T) 1 % FeS (K) 3 % NaCl 1 % $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	0.1719	13,928		
3	40/60	28 % FeS (T) 8 % FeS (K) 4 % NaCl	0.1875	1,721		

\* Cr – crystal, X –  $X$ -ray amorphous.

\*\* T – tetragonal FeS (mackinawite) and C – cubic FeS.

$hkl$  – crystallographic indices (Miller indices) characterizing the arrangement of atomic planes in the crystal (these are whole numbers equal to the number of parts into which the unit-cell edges  $a$ ,  $b$ ,  $c$  are divided).



in the aqueous phase than in the vapor phase. Moreover, as per [21], a temperature rise from 25 to 80 °C also contributes to an enlargement of crystal compound facets, particularly noticeable in the context of HSC in aqueous environments.

In HSC, corrosion products start to form immediately upon exposure to an aqueous environment containing hydrogen sulfide, a phenomenon observable through visual inspection during experiments. The composition and thickness of these corrosion products are influenced by the operational conditions. Numerous studies under HSC conditions have corroborated that the nature and consistency of the deposits significantly impact corrosion processes [22] and the capability of hydrogen to permeate into steel in aqueous environments [21].

Research documented in [23] indicates that the rate of hydrogen permeation during HSC is influenced by  $P_{\text{H}_2\text{S}}$ , which affects the morphology and structure of the corrosion films formed. Investigations on API X65 pipeline steel in environments containing  $\text{H}_2\text{S}$  have shown that the incidence of hydrogen cracking is contingent on both  $P_{\text{H}_2\text{S}}$  and the pH level [24]. As  $P_{\text{H}_2\text{S}}$  increased from 0.001 to 0.1 MPa, there's a predictable rise in the number of visible microcracks on the steel surface. However, the pH level exerts a more significant influence on hydrogen permeation; in acidic conditions (pH = 3.5), permeation rates surpass those in relatively neutral conditions (pH ranging from 5.5 to 6.5). For example, at  $P_{\text{H}_2\text{S}} = 0.1$  MPa and pH = 5.5, the amount of hydrogen absorbed by the steel decreased and, consequently, the effect of hydrogen cracking on the steel surface decreased. The authors attribute to the formation of denser and more uniformly distributed corrosion products (FeS) at the highest  $P_{\text{H}_2\text{S}} = 0.1$  MPa, which impede hydrogen permeation. Additionally, the formation of mackinawite may decelerate the anodic process of HSC, thereby slowing down the associated electrochemical reaction of hydrogen formation. Another study [25] has noted a reduction in hydrogen diffusion over time, resulting from the development of denser corrosion layers that obstruct the anodic-cathodic process of HSC on pipeline steel.

Visual examination of samples post-exposure to the MB2 environment (Table 3) reveals the formation of blisters of varying sizes on St20 steel in the absence of  $\text{H}_2\text{S}$  protection measures, like corrosion inhibitors, under identical conditions (11). This variability in blister formation is likely due to the unique microstructural features of St20 steel, which exhibits a notably uneven distribution of the pearlite phase. Within the ferritic matrix, pearlite manifests as both discrete particles and sizeable clusters. Such microstructural diversity creates varying sizes of hydrogen “traps,” thereby affecting the morphology of the resulting blisters.


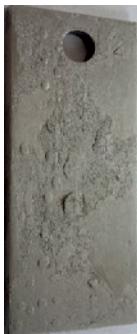
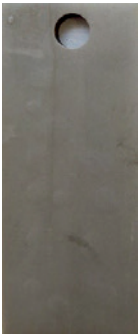
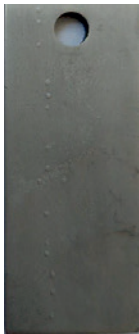




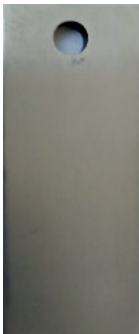
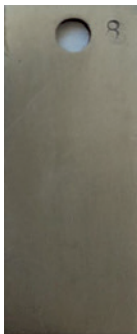
Recent developments in the pipeline transportation of hydrogen, including blends of hydrogen with methane, have seen significant interest. According to a review in paper [8], studies from abroad conducted over the past decade or so reveal that existing data on the operation of main gas pipelines for transporting methane-hydrogen mixtures are not comprehensive. This is primarily because the fundamental parameters, such as strength and steel composition, differ significantly, complicating the identification of consistent patterns regarding hydrogen's impact on steel. Furthermore, the operational performance of these pipelines has been deemed inadequate for future needs. The hydrogen content in these methane-hydrogen mixtures varies from a minimal 2 – 3 % to a maximum of 20 %, with transportation distances spanning several tens of kilometers, and the total pressure not surpassing 1 MPa. The authors of [8] suggest that the observed low performance is attributed to the utilization of older main gas pipelines, which were subject to operational limitations. This has led to varied data regarding the safe hydrogen content or the critical  $P_{\text{H}_2}$  value in the hydrogen-methane mixture. However, there is a consensus among researchers [26 – 27] that a higher  $\text{H}_2$  content could exacerbate the wear on pipeline steel, adversely affecting its plasticity, ductility, and resistance to crack propagation.

Furthermore, it was previously noted [28] that  $\text{CO}_2$  is commonly encountered at oil and gas facilities and may be transported alongside  $\text{H}_2$  through gas pipelines. This scenario becomes particularly relevant when free moisture is present, such as during condensation [4]. In such cases, the chemical interactions involving  $\text{H}_2$  (with  $\text{CO}_2$  present in the natural gas) can act as an additional source of reagents that initiate internal corrosion, further complicating the challenges associated with transporting these gases. The research cited in [9] identifies lower carboxylic acids as intermediate products of chemical interactions that acidify the environment, posing a corrosive threat to steel and potentially enhancing the cathodic process of steel hydrogenation [1]. During the transport of methane-hydrogen mixtures,  $\text{CO}_2$  can be present as an impurity, with up to 2.4 % allowed in natural gas through main gas pipelines. Studies [29] have demonstrated that the presence of both  $\text{H}_2$  and  $\text{CO}_2$  simultaneously increases the rate of fatigue crack growth more than in an environment containing only hydrogen. This suggests a synergistic effect of  $\text{CO}_2$  on hydrogen embrittlement, yet the mechanism behind this interaction remains poorly understood and warrants further investigation.

Subsequent experiments were conducted to examine wire plasticity in an  $\text{H}_2$  environment akin to the hydrogen sulfide conditions previously discussed. It was found (Table 4) that in an aqueous environment (0.5 % NaCl solution), steel plasticity is on average 50 – 60 % lower when 50 – 60 % lower when  $\text{H}_2$  and  $\text{CO}_2$  are present during

**Table 3. Appearance of the samples after testing in the MB1 environment and protective properties of the corrosion inhibitor (numbering of the experimental conditions is given in Table 1)**

**Таблица 3. Внешний вид образцов после испытаний в среде MB1 и защитные свойства ингибитора коррозии (нумерация условий эксперимента приведена по табл. 1)**

9	10	11		12
Without the corrosion inhibitor				
				
With the corrosion inhibitor				
				
$K = 0.013 \text{ mm/yr};$ $Pl = 8.8 \%$	$K = 0.026 \text{ mm/yr};$ $Pl = 4.1 \%$	$K = 0.038 \text{ mm/yr};$ $Pl = 12.9 \%$		$K = 0.070 \text{ mm/yr};$ $Pl = 21.7 \%$

together. However, these tests did not show any significant effect of  $\text{CO}_2$  on hydrogen permeation (Table 4), indicating that more research is needed in this area.

Interestingly, in the vapor phase of  $\text{H}_2$  and  $\text{CO}_2$  (without contact with water), no decrease in steel plasticity was observed, similar to conditions where the water is saturated with  $\text{CO}_2$  only. This suggests that the tests did not reveal any impact of hydrogen on steel's plastic properties in the vapor phase (Table 4) possibly due to the short duration of the tests (120 h). In contrast, hydrogenation and subsequent hydrogen embrittlement of steel occur much more rapidly in an  $\text{H}_2\text{S}$  environment (Table 1) than with  $\text{H}_2$  alone. According to [30], the increase in hydrogen cracking in an  $\text{H}_2$  environment is linked to the greater amount of hydrogen absorbed by the steel, with the time required for hydrogen to permeate into steel's dislocations being a critical factor. Thus, the duration of hydrogen exposure is a significant aspect to consider in future experimental designs.

The paper [31] further elucidates the impact of hydrogen on gas main pipelines, noting a reduction in plasticity and crack resistance of pipe steels by 20 – 60 %, and a significantly higher crack propagation rate. Simultaneously, the risk of hydrogen embrittlement increases as the hydrogen concentration in the hydrogen-methane mixture rises, leading to a corresponding increase in  $P_{\text{H}_2}$ . Research cited in [32] identifies a critical  $P_{\text{H}_2}$

together. However, these tests did not show any significant effect of  $\text{CO}_2$  on hydrogen permeation (Table 4), indicating that more research is needed in this area.

**Table 4. Results of the studies in 0.5 % NaCl solution on change in plasticity of Sv08A wire after autoclave tests**

**Таблица 4. Результаты исследований в 0,5 %-ном растворе NaCl по изменению пластичности проволоки Св08А после автоклавных испытаний**

Phase	$P$ , MPa		$Pl$ , %	
	$\text{H}_2$	$\text{CO}_2$	without the inhibitor	with the inhibitor
Aqueous	0.81	1.78	50 – 60	0
Vapor	0.81	1.78	0	0
Aqueous	1.40	2.13	60 – 64	0 – 16
Vapor	1.40	2.13	0 – 18	0
Aqueous	0.69	0.05	50 – 59	0
Aqueous	–	1.78	0 – 6	0



range of 0.05 to 0.1 MPa for austenitic stainless steel type 304SS, beyond which the material begins to exhibit embrittlement at room temperature in an inert gas environment containing hydrogen.

Studies [29; 31] have shown that hydrogen presence shifts the dominant failure mode of steel from ductile to brittle, thereby altering its mechanical properties. It's highlighted in [31] that both  $H_2$  and  $H_2S$  environments can reduce the plasticity of steel and intensify hydrogen embrittlement. Specifically, steel samples with a streaked ferritic-perlitic structure exhibited lower resistance to a hydrogen-methane mixture than those with a more uniform ferrite-bainite structure. Further findings [33] indicate that hydrogen crack initiation in X42 pipeline steel, exposed to a hydrogen ( $P_{H_2}$  ranging from 0.5 to 10 MPa) and natural gas mixture, tends to occur at the ferrite/perlite interface. This interface is a critical site for hydrogen diffusion, especially under local stress or strain along grain boundaries.

Mitigation strategies against the detrimental effects of hydrogen include modifying the steel's microstructure to reduce factors that contribute to  $H_2$  accumulation and employing corrosion inhibitors. Among the primary defenses against hydrogen sulfide cracking (HSC) is the use of corrosion inhibitors.

One of the main means of protection against HSC is the use of corrosion inhibitors. However, it should be noted that under such conditions the impact of hydrogen sulfide embrittlement on steel pipes and equipment seriously complicates the selection of potential corrosion inhibitors, in addition to aggravating corrosion [34 – 35].

Technologies for administering corrosion inhibitors encompass injecting them into the aqueous environment or forming an inhibitor coating to safeguard steel in the vapor phase. The conducted experiments reveal (Table 3) that the vapor-phase inhibitor coating can effectively protect the steel using the specified corrosion inhibitor (corrosion rate below 0.1 mm/yr), but it fails to entirely prevent defect formation on the steel's surface. Meanwhile, steel hydrogenation was found to be minimal: hydrogen uptake was 4.1 % at 30 °C and increased to 21.7 % at 90 °C. In contrast, inhibitor coatings from other chemicals not discussed in this document provided even less protection against hydrogen sulfide cracking (HSC) (corrosion rates ranging from 0.187 to 0.303 mm/yr) and hydrogenation (hydrogen uptake between 34 and 64 %), resulting in numerous pits on the steel surface.

When the most effective inhibitor was introduced into the aqueous environment, overall corrosion damage was minimal ( $K = 0.013 - 0.038$  mm/yr), and steel retained high plasticity ( $Pl = 8.8 - 12.9$  %) (Table 3). However, an initial inhibitor concentration of 100 mg/l proved to be insufficient at 90 °C, as localized damage occurred

on the steel surface. Increasing the inhibitor concentration in the aqueous phase by 2 to 3 times successfully prevented localized corrosion on the steel surface at elevated temperatures during the test (Table 3).

The occurrence of increased pitting corrosion might be attributed to either an inadequate concentration of the corrosion inhibitor, preventing the formation of a uniform protective layer on the steel, or a low adsorption rate on the metal surface compared to that of reactive iron sulfide (FeS). According to the study referenced in paper [34], the competitive adsorption between iron sulfide and the corrosion inhibitor on the steel surface might undermine the effectiveness of the inhibitor film.

Additionally, employing corrosion inhibitors in an aqueous environment saturated with  $H_2$  and  $CO_2$ , was also effective in preserving the plasticity of steel (Table 4).

Research aimed at improving steel properties and enhancing their resistance to hydrogen permeation is also ongoing. The paper [36] gives a positive example when the homogeneous ferrite-bainite microstructure of steel with enhanced resistance to hydrogen cracking is formed. The regulation of the thermal modes of steel quenching and tempering enables obtaining the metal structure with such levels of microstresses and dislocation density that resistance to cracking in the  $H_2S$  environment can be increased [37]. The studies [12] proved that the ratio of ferrite and pearlitic components can be changed by increasing the temperature from 850 to 1150 °C as API X65 pipe steel is formed. The content, stability, and sizes of the faces of ferrite grain increase, while simultaneously, the pearlite content in the steel decreases from 15 to 2 %. As the proportion of ferrite in the steel increases, there is a notable reduction in both cathodic and anodic reaction rates within  $H_2S$  environments, alongside a decrease in the accumulation of hydrogen within “traps”. To bolster the resistance of structural steels to cracking when exposed to  $H_2S$  environments, a comprehensive strategy is employed. This strategy involves the modification of steel through the addition of calcium and rare-earth elements, in conjunction with processes such as quenching followed by tempering. These modifications are aimed at preventing the formation of CANMIs, like iron sulfides, within the steel matrix. By inhibiting the development of these inclusions, the approach effectively reduces the emergence of microstresses in their vicinity. Consequently, this leads to a decrease in microcrack formation, thereby diminishing the risk of hydrogen-induced cracking in the steel.

## CONCLUSIONS

Research analysis and literature review reveal that steel's plasticity is adversely affected by hydrogenation in hydrogen sulfide environments, such as those encoun-

tered in gas fields, as well as in the presence of molecular hydrogen, whether alone or combined with other gases. The conditions prevalent in H<sub>2</sub>S-containing gas fields pose a significant aggressive influence on the cracking of pipelines and equipment constructed from carbon and low-alloy steels. This susceptibility to hydrogenation is manifested through the development of cracks and blisters on the surfaces of various steels. The propensity for hydrogen to permeate and be stored in steel is heightened and influenced by microstructural inhomogeneities, including CANMIs, as well as the distribution and dimensions of ferrite-perlite components within the steel. It has been noted that the corrosion film that forms on steel in vapor phase environments is significantly thinner than that formed in aqueous conditions. In environments that are acidified by acetic acid, the cubic form of iron sulfide emerges alongside mackinawite (tetragonal FeS, the primary corrosion product), resulting in a less compact film that diminishes its protective capabilities. The physical characteristics of these deposits, such as their density, compactness, presence of pores, and thickness, play a crucial role in determining their effectiveness as barriers against both HSC and the permeation of hydrogen into the steel. Employing corrosion inhibitors has been shown to effectively preserve the plasticity of steel at adequate levels in environments containing H<sub>2</sub> and H<sub>2</sub>S, including scenarios where CO<sub>2</sub> is also present.

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