Stress corrosion cracking of pipeline steels in near-neutral-pH solutions: the role of mechanochemical and chemomechanical effects

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Abstract. The article attempts to summarize the results of modern experimental studies and numerical modeling of mechanochemical and chemomechanical processes occurring on the surface of pipe steels and at the top of the crack under the simultaneous effects of stresses / strains and corrosion media. The influence of these processes on the mechanism and kinetics of corrosion cracking of pipe steels in near-neutral aqueous solutions is discussed. The criteria for the quantitative assessment of the influence of mechanochemical and chemomechanical effects (MCE & CME) on the stress corrosion cracking (SCC) of pipeline steels are considered. The analysis of research methods for the study of MCE and CME was carried out with the aim of further developing a unified methodological approach to assessment and quantification in predicting SCC in neutral media.

Stress corrosion cracking (SCC) of pipeline steels is one of the most important problems in the countries that have the extensive systems of high-pressure buried gas pipelines [1–12]. Analysis of the published data showed that failures of the SCC occurred in gas pipelines operating in different continents and climatic regions and built of pipes of different diameters, and according to the standards of different countries pipe steels had significantly different chemical compositions and mechanical properties; the only constant condition for the development of this process was the access of the aqueous medium to the surface of the metal of the pipes due to disbandment of the tape coating [1, 4–7, 10, 11].

Depending on the composition of the electrolyte under the coating, two main types of SCC of pipeline steels are distinguished: intergranular cracking in concentrated carbonate electrolytes with high pH (8…10) and transgranular cracking in dilute electrolytes with near-neutral pH (5,5…7,5). The qualitative characteristics of the main types of SCC are presented in a large number of original works and reviews [1, 4–6, 8, 11].

To date, it has become apparent that it is impossible to apply the equations (or criteria) of electrochemistry and fracture mechanics separately to describe the kinetics of the SCC pipeline steels, since the process occurs under the simultaneous action of electrochemical and mechanical factors. Secondly, the mathematical (quantitative) description of the SCC models of pipeline steels is possible based on the results of experimental modeling of various stages, but the disadvantage is that the obtained empirical coefficients and dependencies cannot be used for a wide range of pipes laid in soils with different component composition.

It seems that a more realistic approach today is to divide off SCC pipeline steels into separate significant phenomena and study these phenomena separately with using of the results to improve the accuracy of the predictive SCC models of pipeline steels [12]. This approach allows us to describe the SCC process, but quantifying requires a more detailed study of individual effects. This will improve the accuracy of predictive SCC models of pipeline steels.

The fundamental relationships, including thermodynamics and kinetics of interactions between the chemical reactivity of a solid surface and the stress state of the surface layers, have been described earlier [13–15]. The acceleration of chemical reactions by mechanical action (mechanochemical effect – MCE) and the increase in near-surface plasticity caused by chemical reactions (chemomechanical effect – CME) simultaneously
The role of MCE in SCC of metals was undoubtedly established, e.g., for stainless steels by Hoar who found that «yield-assisted anodic dissolution of 18-8 chromium-nickel steel is clearly a conjoint mechano-chemical phenomenon, not the result of consecutive action of separate mechanical and chemical processes» [17]. Additionally, it was found [18, 19] that the effect of yielding (plastic deformation) on the rate of the anodic dissolution of metals (Fe, Mo, Ni, and Cu) in acid solutions was much more pronounced than that of the elastic deformation. The CME [13–15] is the change in the physico-mechanical properties of a metal under the influence of chemical (electrochemical) reactions on its surface. In the literature this effect is paid less attention than the opposite effect, which develop at the tip of stress-corrosion cracks resulting from synergistic interaction between them, should be more deeply investigated to prevent the failure of main gas pipelines. In the following subsections of the review, the authors will try to consider critically the use of MCE methods for studying corrosion under the stress of main gas pipelines and predicting their durability in near-neutral groundwater.

**Theoretical background and experimental verifications of MCE and CME**

The term «mechanochemistry» was introduced by Wilhelm Ostwald [16] at the beginning of the XX century. The effect of mechanical deformation of a solid on the course of chemical reactions is one of the oldest empirically observable facts, e.g. in procuring fire.

The main cause of the CME is an increase in the activity and a decrease in corrosion resistance of a solid. The Δφ₀ value for a solid system of positive ions due to the presence of the mechanical action of positive or negative elastic stresses (their absolute value ΔP > 0) and plastic deformations of a solid can be found from equations (1) and (2), respectively [13]:

\[ \Delta \phi_0 = -\frac{\Delta PV_n}{zF} \]  
\[ \Delta \phi_0 = -\frac{n\Delta \tau R}{\bar{\alpha}k N_m zF}, \]

where \( V_n \) – molar volume; \( z \) – charge-transfer valence; \( F \) – Faraday constant; \( n \) – number of planar dislocations in a pile-up; \( \Delta \tau \) – resolved shear stress; \( R \) – universal gas constant; \( \bar{\alpha} \) – coefficient describing mobile dislocation density (10⁶…10¹¹ cm⁻²); \( k \) – Boltzmann’s constant; \( N_m \) – maximum possible dislocation density considered as one mole of dislocations.

As experimental verification of MCE, the effect of plastic strain on kinetics of cathodic and anodic processes on wire specimens of low-carbon steel was investigated [13]. The increase in anodic increment \( \Delta i_a \) before the onset of easy glide is proportional to the growth of strain hardening \( \Delta \tau \) in the stress range between the elastic limit and the beginning of easy glide (fig. 1). Summing up the theoretical analysis of the effect of plastic deformation on MCE, one should point out three...
stages of strain hardening curve. In the stage I new dislocations appear at easy glide without planar pile-ups formation. MCE does not increase essentially and may even decrease due to relaxation of existing pile-ups. Stage II is characterized by intense strain hardening at the stress increase, and planar pile-ups appear leading to sharp increase in MCE in accordance with equation (2). Dislocation glides and cross slips lead to their uneven distribution, resulting into numerous dislocation tangle and pile-up groups that collectively contribute to the strain-hardening of the polycrystalline metal. Stage III as a final stage of dynamic recovery is characterized by planar pile-ups destroying, cell walls (sub-boundary) are formed leading to the sharp decrease in n values (see eq. (2)), strain hardening is weakened, and MCE significantly decreases.

To study the CME on the metal surface, various electrochemical, physical and mechanical methods have been used, such as measuring nano- and micro-hardness under conditions of anodic polarization [13, 20, 21]. Experiments conducted on iron single crystals and steels confirmed the presence of the CME in microhardness tests [13]. The reduction of the nano-hardness under anodic polarization comparing to air was confirmed also for pure iron [20].

Nevertheless, until now, numerous researchers connect corrosion cracking with the processes of film formation and destruction at the tip of growing crack, i.e. with active-to-passive transitions [21–25]. However, selective dissolution of metal in the crack tip required for its growth may be caused by other reasons, which are not necessarily connected with competing processes of passive film rupture and recovering [26]. In this paper, authors consider other possible processes that affect the dissolution of steel under stress (i.e., MCE), or mechanical behavior as a result of chemical/ electrochemical interactions (i.e., CME) in a near-neutral pH (NNpH) aqueous medium, and, accordingly, the development of individual stages of SCC.

**MCE and CME during SSC of pipe steels in pH-neutral aqueous media in view of the sequence of the process stages**

It is generally recognized that the stress corrosion cracking of pipe steels is a multi-stage process, which includes at least four main stages: the incubation period, the initiation of cracks, the stable development of cracks to a critical size, and the accelerated accidental destruction [1, 6, 9, 12]. Let us consider the successive stages of the formation and propagation of the cracks from the point of view of the possible manifestation of MCE & CME using as an example a well-known scheme of the time-dependent crack velocity [1, 24, 12]. At stage «0» (the incubation period) metal dissolution enhanced by stress and plastic deformation occurs in NNpH solutions with the formation and growth of corrosive pits and «pitting-like» damage, formed near structural inhomogeneities (non-metallic inclusions, pearlitic colonies, slip bands, etc.) and near mechanical damage (scratches, dents or tears), which are stress concentrators on the surface of steel [6, 9, 27–30].

Increased corrosion of metal caused by the simultaneous effects of stresses / deformations and the environment can be explained from the standpoint of the mechanochemical concept discussed above. Recently, some expressions of mechanochemistry, in particular, for the change of Δφ0 (see eqs. (1, 2)) and Δi₄ (see further eq. (3), p. 10) of elastically and plastically stressed metals, were taken into account in study of stress corrosion of pipeline steels in NNpH solutions [29–37].

The effect of mechanical factors on parameters of electrochemical reactions (i.e., MCE) appears, e.g., in the change in an open circuit potential (OCP) of pipe steels during the slow strain rate test in a 0,5M Na₂CO₃ + 1M NaHCO₃ solution [38] and in the NS4 anaerobic solution (pH 6,8) [35]. It was established that for X80 steel in a carbonate-

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**Fig. 1. The effect of strain ε and strain rate ε̇ on anodic current density Δi₄ for low-carbon wire steel in 3,5M H₂SO₄ [13]:**

| ε̇, s⁻¹ | Δi₄, mA·cm⁻² |
|--------|--------------|
| 0,0019 | 0.05         |
| 0,0062 | 0.10         |
| 0,0114 | 0.15         |

σ, MPa

0 0,05 0,10 0,15

0 5 10 15 20

Strain ε, %
bicarbonate solution open to air at the chosen strain rate ($\dot{\varepsilon} = 10^{-6} \text{ s}^{-1}$) OCP was monotonically shifting in a positive direction at strain increasing from 0 to 0,070 due to the continuous formation of a passive film without its destruction even in the field of plastic deformation [30]. As contrary to this fact, in the NS4 anaerobic solution using the same strain rate and strain range X70 steel shows the OCP shift to the negative direction with increasing strain. The effect of plastic deformation on the electrochemical parameters is attributed to three main aspects of MCE: an increase in the electrochemical thermodynamic activity of steel, a change in the density and distribution of dislocations, and an increase in surface roughness [29]. Similarly to B.T. Lu, et al. and Z.Y. Liu, et al. [39, 40], authors call the process of localized surface plasticity due to anodic dissolution which could increase the mobility of dislocations (CME) as «corrosion-facilitated plasticity» [29]. In this example, the close relationship between MCE and CME is clearly manifested. Plastic deformation due to MCE causes a change in the electrochemical parameters (shift of an open circuit potential), contribute to the absorption and permeation of atomic hydrogen into steel, as well as anodic dissolution, especially in localized active centers, which serve as nucleation sites for cracks [41]; in turn, under certain conditions (low atomic hydrogen concentration, etc.), hydrogen can cause the hydrogen-induced plasticity (i.e., CME).

The effect of very small initial plastic deformation of X80 steel ranged from 0,001 to 0,008 (the yielding plateau) on corrosion behavior in 0,62M NaCl was investigated in a four-point-loading apparatus, in which the exact strain values were obtained using the adjustable bolt and measured by strain gauges [30]. At strain closed to 0,0055 a six-fold increase in the corrosion current density ($i_{cor}$) was observed. Such a jump in $i_{cor}$ was explained by an avalanche increase in the number of dislocations (multiplication), which gradually turn into pile-ups of dislocations. Taking into account eq. (2), the authors explain such a jump in $i_{cor}$ by a significant increase in the number of dislocations $n$ and resolved stress $\Delta\sigma$, although the yield plateau is characterized by a constant value of $\Delta\tau$ [30]. Similar dependencies were obtained for the same steel in an in-situ tensile test combined with a potentiodynamic polarization test under the given potential (OCP + 100 mV) in a sulfate-reducing bacterial solution with pH $\approx 7,1$ [37]. At the beginning of the yielding plateau a huge jump in $\Delta\tau$ was detected from 0,18 to 10 $\mu$A due to destroying the dislocation pinning and their multiplication (a jump in $n$, see eq. (2)). The further slight decrease of the anodic current density, as the authors explain [37], is due to a decrease in the generation velocity of the Lüders bands (localized bands of plastic deformation in metals experiencing tensile stresses) [37]. The same phenomena have been observed in literature [13, 33].

Mechanochemical behavior of X100 pipeline steel under uniaxial elastic stress in an NNpH solution was estimated [32]. By substitution of the relevant parameters and the maximum uniaxial stress of $\Delta P = 600 \text{ MPa}$ ($\sigma/\sigma_{yield} = 0,75$, where $\sigma_{yield}$ – yield strength) into eq. (1), it was calculated that the theoretical change of $\Delta\phi_{th}$ was 7,4 mV. The experiment showed that the change in the electrode potential ($\Delta\phi$) was significantly less than $\Delta\phi_{th}$. This is due to the significant electrochemical heterogeneity of the surface (places with predominant anodic or cathodic reactions), as a result of which the only average value of the OCP is measured, while the eq. (1) refers to the local potential of the electrode, which varies much more significantly.

Additionally, when there is a local plastic deformation, the local corrosion activity is increased remarkably. With static elastic stress, which is well below the yield strength, local plastic deformation is possible, e.g., if there are some metallurgical defects, pits, etc. [13, 33, 36, etc.]. For example, when the solution contains an aggressive chlorine ion Cl–, macroelastic deformation, which is applied to bainitic and ferritic low carbon steels using both «soft» constant load and «hard» load using the slow strain rate testing (SSRT) method, causes stress accelerated corrosion due to MCE with pits formation [36]. When the critical stress exceeds 0,5 and 0,7 $\sigma_{yield}$ for ferritic and bainitic steels respectively, the applied mechanical energy will cause microplastic deformation of the macroelastic deformed steel, which generates at grain boundaries and then extends into the grains. Due to the stress concentration in the pits caused by chloride ion, the potential change of $\Delta\phi$ under loading from 0 to 0,5 $\sigma_{yield}$ was calculated to be 16,4 mV (see eq. (1)), which is smaller than the experimental value 33,8 mV. A large number of local plastic flows generated at grain boundaries due to enhanced dislocation motion is the reason which causes the break point in MCE [36]. In turn, additional anodic dissolution in regions of pits and
Plastic strain would increase the MCE significantly, coupling current density and electrochemical impedance spectroscopy (EIS) measurements. L.Y. Xu et al. [33] suggested that, in reality, a non-uniform distribution of plastic stresses and strains on pipelines would cause quite different corrosion activities on the steel. This could be the reason to initiate preferential localized corrosion and even cracks [1, 7]. On the base of a number of dependencies of mechanochemistry [13–15] the shift of electrochemical corrosion potential as a function of plastic strain ($\varepsilon_{pl}$) was established for the different values of initial density ($N_0$) of dislocations prior to plastic deformation [33]. The calculation of the shift of corrosion potential shows that $N_0$ increasing on one order of magnitude from $10^8$ to $10^9$ at plastic deformation of 0,005 and 0,035 causes the shift of $\Delta\varphi_i$ in the negative direction from $-4$ to $-20$ mV$_{SCE}$ and from $-16$ to $-42.5$ mV$_{SCE}$ respectively. The indicated results on the assessment of dislocation densities obtained by computational methods require more detailed study and experimental confirmation in the case of SCC of pipe steels in media with a pH close to neutral.

According to L.Y. Xu and Y.F. Cheng [31], both the anodic and cathodic reactions should be taken into account at the analysis of the mechanochemical corrosion of plastically strained steel. By finite element (FE) method and using localized electrochemical impedance spectroscopy on the samples of X100 steel with various widths it was shown that there were quite different corrosion activities on the steel due to a non-uniform distribution of plastic strains. The FE simulation included (i) elasto-plastic solid stress analysis of the pipe, (ii) electrode potential and current density analysis at the steel/solution interface, and (iii) simulation and analysis of MCE, i.e., the interaction of mechanical parameters and electrochemical corrosion behavior of the steel in solution. L.Y. Xu and Y.F. Cheng [31] assumed that the pipe steel was in an active dissolution state. The equilibrium potentials of anodic reaction depending on elastic and plastic strains were calculated using eqs. (1) & (2), meantime, for describing of MCE on cathodic reaction ($i_c$) a semi-empirical expression was derived:

$$i_c = i_{0c} \cdot 10^{\frac{\sigma_{Mises} k T}{R T} \cdot F(b)} ,$$

where $i_{0c}$ is exchange current density of hydrogen evolution on X100 steel in the absence of external stress/strain; $\sigma_{Mises}$ is von Mises stress calculated from FE; and $b_i$ is cathodic Tafel slope [31].

The most important findings obtained using the FE model are the various effects of tensile strain and depth of corrosion defect on stress distribution. While tensile deformation leads to an overall increase of stress through the pipe wall, the increasing corrosion defect depth causes a more concentrated stress at the defect center, which serves as anode, and the sides of the defect serving as cathode. Local plastic deformation due to increased tensile strain or the corrosion depth leads to anodic dissolution in the center of the defect, where local corrosion activity increases significantly.

Subsequently, this FE model was supplemented by the study of time-dependent MCE at corrosion defect, enabling prediction of the defect growth over a long-term time period [34]. The time dependence of local stress and anodic current density at corrosion defect can be featured with three stages, namely: a negligible corrosion in elastic region; a slow increase of both stress and anodic current density under mild plastic deformation; and a rapid increase of both stress and anodic current density under a high local plastic deformation. The accelerated corrosion at stressed defects (i.e., MCE) can be mitigated effectively by reducing operating

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1. SCE = saturated calomel electrode.
pressure and application of cathodic protection on pipelines. The disadvantage of this work is the lack of consideration of residual stresses on the pipe surface. Thus, it was established [12] that increased residual deformations measured by fiber-optic sensors when loading pipes with pressure were observed in areas with shallow corrosion defects and SCC cracks (depth up to 1.5 mm). Therefore, one should expect a high rate of steel dissolution even at small sizes of defects due to the influence of residual operational stresses in the surface layer.

A numerical method for studying mechano-chemical processes in the pitting and grooving corrosion of steel structures under external and internal stresses was proposed [35]. Numerical simulation of these processes allows determining local surface areas with an increased level of stresses and deformations and, accordingly, identifying localized areas of accelerated dissolution of stressed metal (mechanochemical corrosion), and quantitatively describes the increase in dissolution current.

According to the analysis of the literature, MCE plays a dominant role in the formation of pits, which are the sites of cracking. It is generally accepted that the main parameter determining the formation and rate of NNpH SCC microcracks (stage I) are the residual tensile stresses in the surface of pipes, the effect of which is added to the applied operational stresses and weakens as the depth of the crack increases [9, 12]. As a result, the total tensile stresses on the surface of the pipe in places of local corrosion defects can reach the \( \sigma_{\text{yield}} \) values of the material [42, 43], and therefore the implementation of the CME and MCE is possible. A strong correlation between residual stress and the presence of NNpH SCC colonies in pipes grades from X52 to X70 was found [44].

Under an applied load (\( \sigma_{\text{appl}} \)), which was very close to the yield point, the crack initiation was really observed in pipe steels of X70 and X80 grades [45, 46]. As a result, NNpH SCC was observed for 278 days at a \( \sigma_{\text{appl}}/\sigma_{0.2} \) ratio of 0.999 (where \( \sigma_{0.2} \) – conditional yield strength), while at a ratio of 0.972 only pitting and cracks without fracture of the specimen were observed [45]. Similarly, cracks could originate and propagate in X80 steel at \( \sigma_{\text{appl}} > 95 \% \) of \( \sigma_{0.2} \) [46].

The kinetics of further development of the SCC at this stage is determined by the aggressiveness of the near-pipe electrolyte, the level of residual stresses, structural and textural features in the surface layer of the pipe; and to a lesser extent it depends on the operational loads. The applied pipe manufacturing techniques lead to formation of areas with different levels of residual deformation on the surface of pipes [42, 43]. Reducing the effect of residual stresses [43, 47] due to the textural heterogeneity of the material can lead to partial or complete cessation of destruction [42, 48]. Considering that determination of the exact value of residual stresses in the metal of a pipe is difficult and requires further study, and macro-properties of the material (mechanical characteristics) do not fit to describe the development of shallow (short) cracks due to their variation even within one pipe [49], stage I requires more detailed study.

It appears that the CME can contribute in the process of crack formation on pipeline steels in neutral pH environments. For example, as indicated [39], both atomic hydrogen and dissolution at the surface discontinuities can increase the surface plasticity of steel (microplastic deformation) contributing to crack initiation and propagation. At this time, as noted [50], the emission of dislocations also plays an important role in promoting both localization of microplasticity and localized dissolution, as well as in maintaining crack sharpness.

The mechanism for the further development of NNpH cracks (stage II, see earlier) is studied in detail. Most researchers try to explain the development of SCC at this stage by various interactions between applied stresses, hydrogenation and local metal dissolution. The influence of these processes on SCC is interrelated, and different authors point out various combinations that have a dominant effect on crack growth.

The majority of researchers are eager to explain the propagation of SCC at this stage by the various interactions between hydrogen charging, and local dissolution of the metal [9, 31, 51]. It has been suggested [39, 52–55] that hydrogen and cyclic loading play a significant role in the cracking of pipeline steel in NNpH electrolytes. Hydrogen-induced plasticity (HIP) [56] and the internal-hydrogen-assisted cracking mechanism are considered as mechanisms of hydrogen influencing crack growth in NNpH solutions instead of the hydrogen environmental-assisted cracking mechanism [55].

A large group of researchers believes that the cause of the growth of cracks in NNpH SCC pipe steels is the synergistic effect of anodic dissolution and hydrogen absorption in the metal [57–59].
An NNpH environment is capable of generating a catalytic surface effect on hydrogen evolution in pipeline steels [60]. Hydrogen evolution markedly depends on the oxidation state of steels [61, 62], and it changes the chemical potential of the steel and enhances anodic dissolution [63]. Thermodynamic justification of the effect of hydrogen concentration on anodic dissolution is described [64–66]. Hydrogen introduced into the steel can promote anodic dissolution and SCC susceptibility, but these ideas contradict the known data on the inhibitory effect of atomic hydrogen on the anodic process of dissolution of iron in acidic environments [67].

It is important to note that the effect of hydrogen on the cracking of pipe steels manifests itself when hydrogen reaches a certain «critical» concentration in metal, which depends on the composition of the corrosive environment, as well as the type and level of the applied mechanical load [68]. However, it was established [69] that the current density of hydrogen penetration into steel in the field conditions did not reach the «critical» values, above which hydrogen embrittlement was observed. Therefore, the development of NNpH SCC with the predominant effect of absorbed hydrogen on crack growth is unlikely, and can be observed with a significant potential shift in the negative direction in solutions containing the hydrogen penetration promoter and/or under specific loading conditions (a certain combination of the stress intensity factor at the crack tip (K), the change of stress intensity factor at the crack tip (ΔK) values and cycle frequency) [70, 71].

Other researchers believe that local anodic dissolution of a metal has a major effect on crack growth in pipeline steel in weakly acidic and near-neutral electrolytes [13, 71–74]. Selective dissolution of metal at the tip of the crack is not necessary connected with competing processes of passive films rupture and recovering. Moreover, in NNpH solutions conventional film rupture–repassivation theory can’t be applied for pipelines, which are in an active dissolution state [11]. It seems, one of the possible reasons of cracking at this stage is the development of MCE and CME at the tip of a crack, as it is presented below.

The corrosion rate at the tip of previously grown fatigue cracks on X65 pipe steel samples was studied at various stress levels in a neutral pH medium (NS4 solution with 5 % CO₂ purge to pH 6,6) [75]. It was shown that at the tip of the crack steel was in a state of active dissolution. There was no significant change (within ±(10…20) mV) in the values of corrosion potential $E_{\text{cor}}$ (~730 mV SCE at the tip of the unloaded crack) at the crack tip under various loads. However, the current density of corrosion increased by more than 2 times with an increase in the applied load up to 95 % of the yield strength of the steel, which indicated an increase in the corrosion rate at the crack tip and, as a result, the implementation of MCE.

The rate of local anodic dissolution of samples of ferritic-pearlite pipe made of X70 steel (yield strength of 650 MPa and tensile strength of 740 MPa) with pre-grown fatigue cracks (2…3 mm length) along the surface of the sample, as well as samples without cracks, was investigated under a constant load of 3000 N in NS4 solution, which was purged with 5 % CO₂+N₂ to pH of 6,8 [76]. It was established by numerical simulation methods that the stress concentration at the tip of the cracks reached values up to 80 % of the yield strength of steel when a tensile load of 3000 N was applied to samples with cracks. It was shown that such a stress concentration almost 3-fold rised the local anodic dissolution rate of steel (and therefore MCE is implemented) at the crack tip. At the same time, the dissolution of the crack tip is accompanied by the formation of a layer of corrosion products on the metal surface, which does not effectively protect the steel from further dissolution due to a loose, porous structure. This leads to the continuous propagation of cracks and an increase in the concentration of stresses at the crack tip, which, in turn, further accelerates the local dissolution of the metal with the time of testing.

It has been suggested [6, 71] that crack growth is possible through anodic plasticity caused by dissolution (i.e., CME), but this effect has not been studied in more detail. Another results can also be considered as manifestation of the CME (in a wider sense than the definition given at the beginning of the «Theoretical background and experimental verifications of MCE and CME» section of this paper) [74]. It has been established that crack growth in X70 pipe steel in a weakly acid electrolyte (pH 5,5) under the action of a static load may slow down due to a decrease in the rate of dissolution of the metal with increasing degree of filling the surface with hydrogen. Thus, an indirect effect of the cathodic reaction of hydrogen evolution on the change in crack growth was shown [74], which can be considered as a special case of CME.
The mechanism of crack growth was considered taking into account the concepts of HIP [56–58]. The effect of HIP can be considered as a special case of the CME. The HIP effect slows down the process of SCC steel in a NNpH medium (NNpH SCC) due to an increase in the plastic deformation zone in front of the crack tip in the potential ranged from –680 to –930 mV_SCE (fig. 2) [40]. However, the detailed mechanism of HIP and its relationship to CME are unclear and require further study.

Further growth of the crack at stage III occurs with the participation of the near-pipe environment under design loads (seasonal ground movements, changes in working pressure), and is also determined by the interaction with adjacent cracks in the colony, with the result that when a certain size and relative position of the crack are reached, linear dimensions increase [6, 27, 77, 78].

After that an increasing effect of variable loads in the pipeline from gas pressure leads to formation and development of a longitudinal main crack until the pipeline collapses. It can be assumed that at these stages of the process the MCE is responsible for the accelerated anodic dissolution of the metal when a load is applied (constant or cyclic), which makes the crack propagate. It has been shown that the MCE has been studied, including some examples of numerical modeling, in more detail than the CME. All authors agree that MCE accelerates the formation of corrosion defects and cracks propagation, however, the assessment of the quantitative contribution in the literature is either absent, or controversial for different authors – the differences are associated primarily with different experimental conditions (sample shape, solution composition, loading conditions, etc.). It is obvious that studies of the CME during the cracking of pipe steels are few, isolated, and require further systematic study, including modeling. In the near future new methods of modeling both MCE and CME should be developed for quantitative prediction of SCC in pipe steels.

In conclusion, it should be noted that further study of MCE and CME in the process of stress corrosion cracking of pipe steels requires more detailed experimental studies in the following areas:

- determination of dislocation densities in pipe steels with SCC steel;
- assessment of the influence of the level of residual deformations / stresses of pipes of different composition and strength classes on the intensity of electrochemical processes;
- determination of the mechanisms of local dissolution of the metal at the top of the crack, alternative to the generally accepted concepts of «film rupture – dissolution»;

**Fig. 2.** Effect of cathodic potential on reduction-in-elongation in NS4 and pH = 4 solutions as compared to air [40]:

- HE – hydrogen embrittlement;
- HIC – hydrogen-induced cracking

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**Concluded remarks**

Analysis of literature shows that the MCE and CME exist when pipe steel is cracking. During the incubation period of a crack initiation near such inhomogeneities as grain boundaries, inclusions, metallurgical defects, etc., the dissolution of the metal enhanced by stress during elastic and plastic deformation takes place in NNpH solutions with formation and growth of corrosion pits, where, undoubtedly, the MCE plays a dominant role. The MCE is responsible for accelerating anodic dissolution at the tip of a crack when a load is applied (constant or cyclic), which makes the crack propagate. It has been shown that the MCE has been studied, including some examples of numerical modeling, in more detail than the CME. All authors agree that MCE accelerates the formation of corrosion defects and cracks propagation, however, the assessment of the quantitative contribution in the literature is either absent, or controversial for different authors – the differences are associated primarily with different experimental conditions (sample shape, solution composition, loading conditions, etc.). It is obvious that studies of the CME during the cracking of pipe steels are few, isolated, and require further systematic study, including modeling. In the near future new methods of modeling both MCE and CME should be developed for quantitative prediction of SCC in pipe steels.

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- determination of the mechanisms of local dissolution of the metal at the top of the crack, alternative to the generally accepted concepts of «film rupture – dissolution»;
assessments of the effect of atomic hydrogen on the plasticization of the surface layers at the tip of the crack;

determination of quantitative criteria to account for MCE and CME in a multi-stage model of pH-neutral SCC pipe steels.

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Коррозионное растрескивание трубопроводной стали под напряжением в растворах с pH, близким нейтральному: роль механохимических и хемомеханических воздействий

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Тезисы. В статье предприятия попытка обобщить результаты современных экспериментальных исследований и численного моделирования механохимических (МХЭ) и хемомеханических (ХМЭ) процессов, протекающих на поверхности трубных сталей и в вершине трещины при одновременном воздействии напряжений/деформаций и коррозионной среды. Обсуждается влияние указанных процессов на механизм и кинетику коррозионного растрескивания под напряжением (КРН) трубных сталей в околоводных и грунтовых условиях. Выполнен анализ результатов экспериментальных исследований МХЭ и ХМЭ с целью дальнейшей разработки единого методологического подхода к оценке и количественному учету при прогнозировании pH-нейтрального КРН.

Ключевые слова: коррозионное растрескивание под напряжением, трубная сталь, механохимический и хемомеханический эффекты.

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