Environmentally assisted "in-bulk" steel degradation of long term service gas trunkline

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Abstract. Comparison of mechanical (characteristics of strength, reduction of area and elongation, impact strength, hardness, fracture toughness), corrosion-mechanical (stress corrosion cracking in the artificial brine and hydrogen embrittlement) properties and parameters of hydrogen behaviour in the X52 steel in as-received state and after long term service are presented in the paper. Hydrogen has been accumulated in the metal of pipes during their exploitation and it was detected by the creation of hydrogen traps during the service. The analysis of a change of the mentioned characteristics together with the results of hydrogen permeation and vacuum hydrogen extraction measurements indicate considerable "in bulk" material degradation of trunk pipeline steel after long term service and essential role of hydrogen in these processes. Therefore the control of pipelines limited the detection of the defects and damage is not sufficient to ensure the safety of operation of gas trunklines.

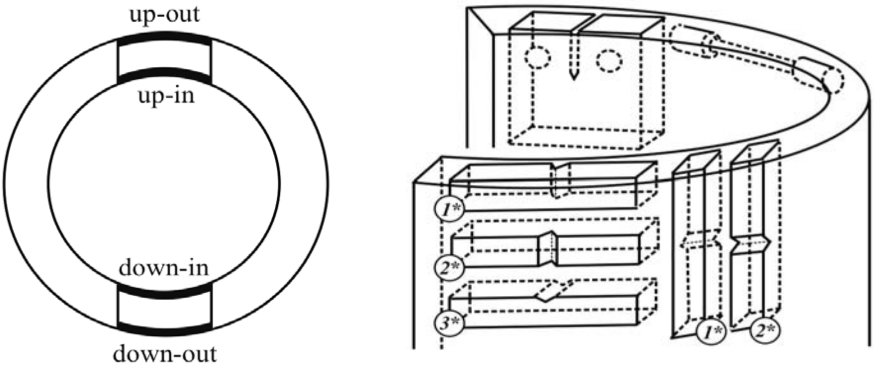
Introduction

A workability assessment of the trunk pipelines exploited for a long time has been mostly based on the monitoring of the corrosion damage of the outer surface of the pipes. However observations of the inner surface of the oil and gas trunk pipelines being in service for long time, revealed the presence of pits, especially numerous on the bottom of the pipe cross-section. In the case of oil trunk pipelines exploited for about 30 years, the substantial decrease in the corrosion resistance, mechanical (especially resistance to the brittle fracture) and corrosion-mechanical in-bulk material properties has been established in comparison to the as-received material [1]. The above findings strongly suggest that not only the pipe surface, but also the bulk material underwent degradation during service. Although the corrosion occurring at the bottom of the pipe cannot itself cause the degradation of the bulk material, the hydrogen evolved in the corrosion processes and entering the metal might be an important factor producing metal deterioration. In the case of the wet gas pipelines, the condensed water accumulates at the pipe bottom [2]. However, gas flow splashes the water deposited at the pipe bottom, thus affecting the other parts of the pipe inner surface [3]. Therefore, the similar processes of metal degradation during the long term exploitation could proceed differently in the metal of the crude oil and of the gas pipelines.

Materials and experimental methods

The pipes made of the ferrite-pearlite X52 steel in as received condition and after service in the onshore section of a gas trunkline after 30 years were studied. The exploited pipes, 275 mm in diameter with wall thickness 10 and 12 mm were compared with as received pipe material (408 mm in diameter, wall thickness 12 mm). The scheme of cutting the specimens from the studied pipes and the code of the samples are shown in Fig. 1.

The program of experimental studies consisted of mechanical, corrosion-mechanical and hydrogen tests. Standard tests evaluating tensile properties, hardness, impact strength, modified tests of fracture toughness and hydrogen extraction were carried out to characterize the material. Additionally, Stress Corrosion Cracking (SCC) tests in the aggressive medium and hydrogen permeation tests were performed to check the susceptibility of materials to SCC, hydrogen embrittlement (HE) and to hydrogen induced blistering cracking (HIBC). The experimental procedure has been described in the reference [4].



a *b*

Fig. 1. Cross-section of the pipes (*a*) and scheme of the cutting of the specimens for mechanical tests (*b*)

Experimental results

Mechanical properties. Mechanical properties were found to be strongly affected by the steel service. In the case of exploited pipes (especially in the case of X52-10 steel) stress-strain curves exhibited the apparent yield plateau not observed for as received steel. The strain-hardening coefficient n (determined from equation $\sigma = a\varepsilon^n$) increased in service, the maximum value corresponded again to X52-10 steel (Table 1). Established difference in ultimate strength (450 – 540 MPa) of the tested steel can not be itself an evidence of their in-service degradation. However the sharp decrease in yield strength of X52-12 steel, practically to the value for pure ferrite, not fitted the standard value for the steel should be noticed. The exploited steels especially X52-10 revealed lower values of RA. The effect of pipe exploitation on the elongation to fracture occurred to be ambiguous: steel X52-10 exhibited the value of that parameter even higher than as-received steel (Table 1). No evident differences in metal degradation have been observed for different places of the exploited pipes.

Code	Place	σ_y [MPa]	σ_{UTS} [MPa]	RA [%]	ε [%]	HRB	n	$J_i/J_{0.2}$ [N/mm]
X52		355	475	72,9	22.7	90	0.59	86/412
X52-12	down	268	451	64.4	20.8	75	0,74	50/127
	up	255	460	62.5	22.9	77		
X52-10	down	362	536	54.6	29.7	81	0,82	37/79
	up	335	538	55.0	28.8	84		

Table 1. Mechanical properties of studied steels evaluated in tests done at RT

The mean values of hardness were not dependent on the specimen position in the pipe: inside surface, outside surface or across wall thickness. However in all cases hardness of the exploited steel was lower than that for as received one and the hardness of *down* parts was lower than that of the *up* parts.

The effect of the specimens cutting place (up, down) on the *J-R* curve was not observed. For all the fragments, the *J* level fitted one curve. Comparison of as-received and exploited steels clearly indicated that the last ones were characterized by strong decrease in fracture toughness and the X52-10 steel revealed more brittle behaviour than the X52-12 one.

As seen in Table 2, the studied steels underwent substantial decrease in the impact strength during the service. Impact strength was stated to depend on the specimen orientation to a pipe generator. KCV level was almost two times higher for specimen cut along the pipe generator.

Concerning the effect of the notch orientation on impact strength, some peculiarity should be mentioned: the X52-10 steel was characterized by a very low KCV level in the case of the “across pipe generator” and of the “3*” notch orientations, when a notch was cut across the wall thickness, cf. Fig. 1.

Code	Place	KCV [J/cm^2]				
		Across pipe generator			Along pipe generator	
		Notch orientation, Fig. 1				
		1*	2*	3*	1*	2*
X52		196	177	169	350	342
X52-12	down	77	73	72	189	198
	up	72	55	64	182	198
X52-10	down	60	65	43	173	195
	up	57	52	48	<145**	<177**

Table 2. Charpy tests data for studied steels

** Specimens with visible stratification along pipe generator were not broken what means that real KCV level is expected to be lower.

*SCC resistance***.** SCC tests of smooth specimens (Fig. 2) did not reveal effect of the aggressive environment when testing in the absence of external polarization (at corrosion potential). However, a noticeable effect was produced by moderate cathodic polarization, which indicated susceptibility of steels to HE. A lower resistance to HE was detected in the case of *down* than *up* parts of exploited material (Fig. 3).

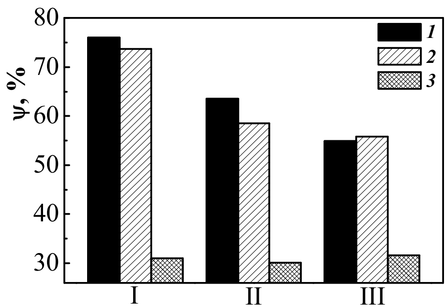


Fig. 2. Averaged values of RA for steels X52 (I), X52-12 (II), X52-10 (III) as measured in air (*1*), in corrosive environment at corrosion potential (*2*) and at cathodic polarization (*3*)

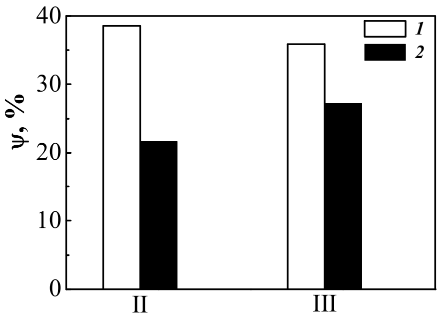


Fig. 3. Susceptibility to HE of *up* (*1*) and *down* (*2*) parts of exploited steels X52-12 (II) and X52-10 (III) at cathodic polarization

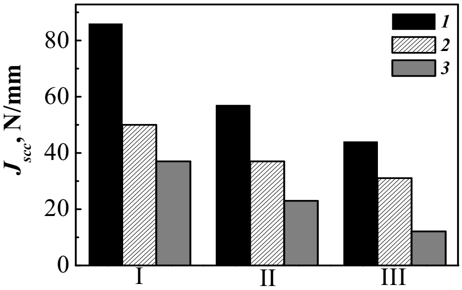


Fig. 4. Crack growth resistance of X52 (I), X52-12 (II) and X52-10 (III) steels in air (*1*), in corrosion environment at corrosion potential (*2*) and at cathodic polarisation (*3*)

Tests on pre-cracked specimens, in disagreement with tests on smooth specimens, indicated (Fig. 4) the susceptibility of investigated steels to SCC in the model environment [5] under open circuit conditions. The application of cathodic polarization additionally decreased the threshold J_{scc} levels of steels. The as-received steel exhibited the maximum resistance to SCC, whereas X52-10 steel was characterized by the lowest J_{scc} level. It should be noticed that no noticeable differences in the SCC resistance was observed for specimens cut from the different parts of the exploited pipes.

Hydrogen behaviour. The highest critical values of i_C* (polarization characterizing susceptibility to HIBC) were exhibited by the as received steel while the lowest were obtained for steel X52-10 (Fig. 5a). For steels X52-10 and X52-12 the lowest values of critical polarization occurred for the down, and especially *down-in* positions. Fig. 5*b* shows the steady state values of current permeated through the studied membranes at cathodic polarization 40 mA/cm^2. The highest permeability (J_∞^{40}) was observed in the case of the as received steel. The lower permeability was recorded for the membranes cut from the *down* parts of pipes and for the *inner* parts of pipe walls, being especially low in the case of the *down-in* parts.

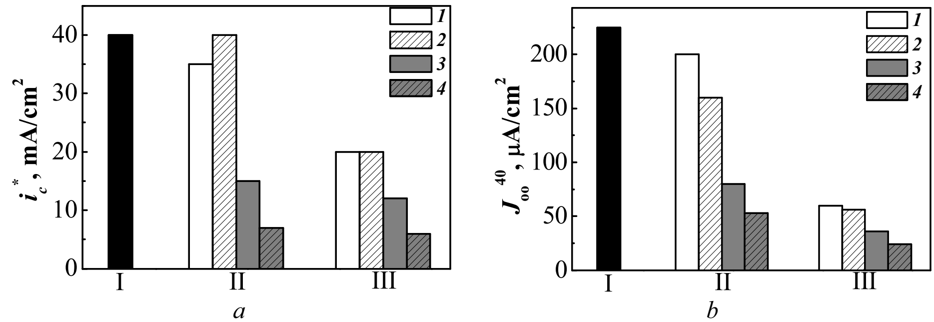


Fig. 5. The critical cathodic current density (*a*) and the steady state hydrogen permeation at cathodic polarization 40 mA/cm^2 (*b*) for steels X52 (I), X52-12 (II) та X52-10 (III) for different places of studied pipes:
1 – up-out, *2 – up-in*, *3 – down-out*, *4 – down-in*

The highest lattice diffusivity was measured in the as received material and the diffusivity decreased for metal being in service (Fig. 6*a*). To some extent, the diffusivity calculated for the *down* parts of exploited pipes was slightly lower than that for the *up* parts, especially in the case of pipe X52-10. The efficiency of hydrogen trapping was higher in the exploited than in as received pipes. As seen in Fig. 6*b*, the trapping efficiency was higher in the case of the *down* and especially *down-in* parts of pipes.

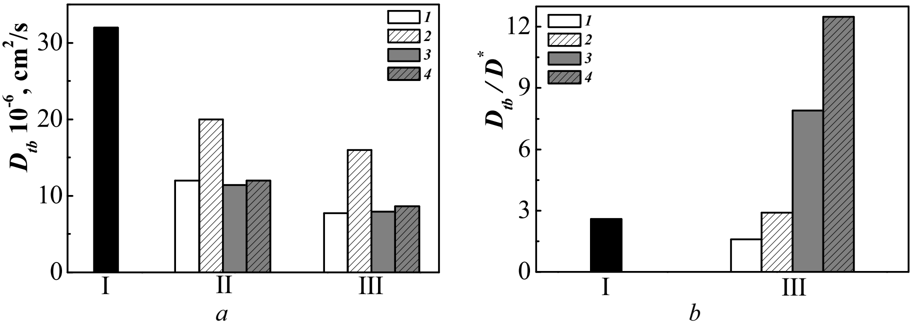


Fig. 6. The calculated values of lattice hydrogen diffusivity (*a*) and the ratio of the lattice diffusivity to the apparent diffusivity (*b*) for steels X52 (I), X52-12 (II) and X52-10 (III) in different places: *1 – up-out*, *2 – up-in*, *3 – down-out*, *4 – down-in*

As seen in Fig. 7*a* the hydrogen extraction from the *down* part is slower than in the *up* part of pipe. The total hydrogen amount desorbed from the exploited materials was higher in the *down* than in the *inner* parts (Fig. 7*b*). For X52-10 pipe, the *inner* and especially *down-in* part contained a higher amount of hydrogen which has been accumulated during exploitation. Table 3 shows that the hydrogen amount desorbed at different temperature changed in the course of the metal exploitation. In the as received steel, hydrogen desorbed mostly at the low temperature. In the case of steels being in service, the most part of hydrogen desorbed at the higher temperature, especially in the case of *down* specimens.

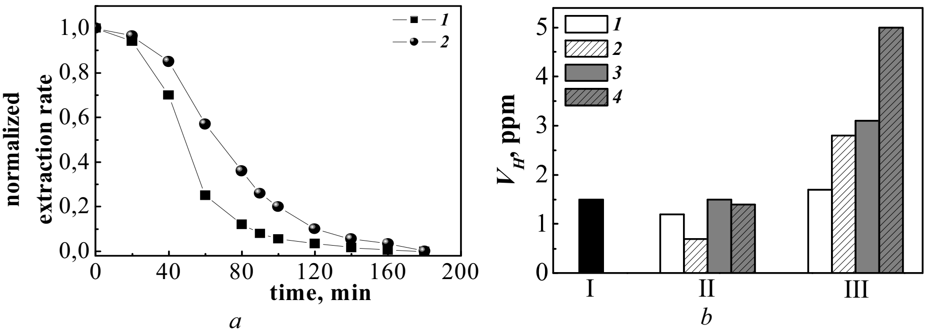


Fig. 7. Hydrogen desorption curves recorded for *up* (*1*) and *down* (*2*) parts of pipe X52-12 at 600°C (*a*) and total hydrogen amount desorbed from different places (*1 – up-out*, *2 – up-in*, *3 – down-out*, *4 – down-in)* of steels X52 (I), X52-12 (II) and X52-10 (III) (*b*).

Code	Place	200^0 C	400^0 C	600^0 C
X-52		1.4	0.07	0.04
X52-10	*up-out*	0.3	0.6	0.8
	down-in	0.15	0.8	4.15
X52-12	*up-out*	0.1	0.5	0.6
	down-in	0.01	1.0	0.4

Table 3. The amount of hydrogen [V_H^n, ppm] desorbed at step by step increased temperature

Discussion

The substantial differences in the mechanical properties of the tested pipe materials could be caused by two reasons: 1) various technological parameters of manufacturing (fusion, thermal treatment, rolling) or 2) in-bulk material degradation being a result of simultaneous influence of the stresses and environment in the course of the long term service. The first reason could have been accepted only with reference to the characteristics of strength and hardness. However the exploited material exhibited an essential change of such strongly regulated characteristics of pipe steels as impact strength and plasticity. The results obtained in the present work confirmed the assumption of some deformation aging undergone by steels during the long term service: the increase in the strain-hardening coefficient. However, there are two peculiarities, which seem not to be in consistence with the above conclusion. The first one: decrease in material hardness due to exploitation was accompanied by a decrease of brittle fracture resistance. Another peculiarity consisted in the different character of the change of parameters of plasticity (ε and RA) in the course of service.

The revealed anomalies in mechanical behaviour of the long term exploited steels can be explained under the assumption that the metal degradation manifested itself not only in the deformation aging but also in the intensive development of damaging (defectiveness) on the micro- and submicrolevels. These two processes produced the ambiguous, sometimes opposite effect on mechanical properties of degraded material. The above state might be modelled by the composite "metal matrix- quasi-pores". The deformation aging strengthened and thus produced the embrittlement of the metal matrix, which manifested itself in an increase in the strain-hardening coefficient *n* and in a decrease in RA. Those changes parameters presumably less sensitive to the "porosity" of material have been quite predictable. On the other hand, the strength as the integral characteristics of composite, being sensitive to the material porosity, could increase or decrease, depending on the dominating process: deformation aging of matrix or development of its damaging. Deformation aging and damage development acted in the opposite direction. Consequently, the opposite effect of service should produce different variations of plasticity: deformation aging of material decreased the RA, while the metal defectiveness increased elongation. Not only plastic deformation but also displacement of multitude defects (pores) influenced the elongation of exploited material, as schematically shown in Fig. 8. Then it should be possible that $d_1 < d_2$ (conditions of embrittlement) would be in agreement with $\Delta_1 < \Delta_2$ (conditions of defectiveness). The degradation leads to the rapid decrease in the impact strength of degraded metal, especially for specimens cut across the pipe rolling direction, cf. Table 2. This may indicate the intensification of anisotropy of the impact strength in the course of exploitation. The above assumption may be also supported by the fact that the specimens cut along the rolling direction from the *up* part of X52-10 steel remained unbroken in consequence of stratification. Reorientation of fracture plane at the impact loading from "across the rolling direction" into the "along the rolling direction" planes has been evidently caused by the stronger degradation of this part of exploited pipe.

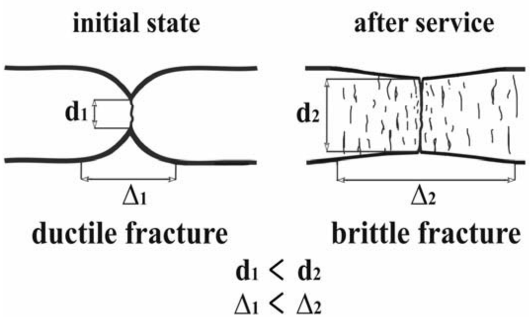


Fig. 8. Scheme of the change of deflection Δ and of residual neck diameter of fractured specimen (*d)* for as-received and exploited states

The assumption of the deep modification of the structure of the long term exploited pipe steel may be supported by the hydrogen measurements. As follows from Fig. 5, the exploitation decreased the resistance to HIBC, which depends on the trapping ability of the metal [5]. An increase in effectiveness of hydrogen trapping has been confirmed by the hydrogen extraction measurements (cf. Table 3).The total hydrogen amount in exploited steels, in contrast to as received material, practically consisted of the high temperature fraction, showing the presence of hydrogen mostly bound in the deep traps. Since the structural defects acted as hydrogen traps, the increase in their number as well as the change of their nature, took place in the course of exploitation.

Established sensitivity to SCC of pre-cracked specimens may suggest the realization of hydrogen mechanism of cracking due to the possible acidification of solution in crack tip. The hydrogen mechanism of SCC has been promoted by the cathodic polarization, which intensified the corrosion crack initiation (SCC tests of smooth specimens, Fig. 2, 3) and propagation (SCC tests of pre-cracked specimens, Fig. 4), as well. The effect of service has been stronger on the crack propagation stage. It should be noted that the degradation of the *down* part was stronger in comparison with the *up* part only on the stage of crack initiation.

The more pronounced degradation in the case of the hydrogen mechanism of SCC has been well correlated with the decrease in critical values of cathodic current density (decrease in resistance to HIBC) in the case of exploited steel. The increased susceptibility of degraded steels to SCC proceeding by HE mechanism has been affected by a developing damage of exploited metal, and because of deep lattice modification [6] which has been supported by the decrease in the hydrogen lattice diffusion coefficient (D_{tb}) being an intrinsic characteristic of the metal lattice (Fig. 6*a*).

The principal question is the possible role of transported medium in the processes of pipes degradation during its 30-years service. In fact, it is possible to assume that a loss of the properties of steels has been caused by influence of mechanical stresses only. However, effect of service on a state of hydrogen, parameters of its diffusion, on HE and on hardness indicated that the *down* parts of pipes were more defective then the *up* ones. It is evident, that effect of aggressive environment on in bulk material degradation is caused by hydrogen, absorbed by metal from transported media during long term service.

Conclusions

1. The decrease in resistance to brittle fracture, revealed by drop of impact strength, reduction in area, fracture toughness and resistance to SCC, to HE and to HIBC of X52 steel exploited for 30 years in gas trunk pipe lines has been established.
2. The anomalies of mechanical behaviour, specific to the in-service embrittlement of metal: a) the decrease in the resistance to the brittle fracture simultaneously with the decrease in hardness, and b) the opposite change of the plasticity parameters, the decrease in RA accompanied by the increase in elongation.
3. The main factor of pipe degradation in the long term service has been assumed to be the microdamage, which has been indirectly confirmed by the increased efficiency of hydrogen trapping, increased ratio of deep hydrogen traps, increase in uniform elongation, decreased hardness and the formation of more intensive binding lips at fracture toughness tests in exploited material.
4. Generally, the degradation was more pronounced in the *down* and especially *down-in* parts of the pipe, which proved the negative effect of transported medium because of the condensation of its aggressive components on the pipe bottom and confirms the important role of hydrogen, absorbed by metal, in bulk material degradation.

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