



# Effect of electrolyte composition on crack growth rate in pipeline steel



A.I. Marshakov<sup>a,\*</sup>, V.E. Ignatenko<sup>a</sup>, R.I. Bogdanov<sup>a</sup>, A.B. Arabey<sup>b</sup>

<sup>a</sup> A.N. Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences, 119991 Moscow, Russia

<sup>b</sup> GAZPROM OJSC, 117997 Moscow, Russia

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## ABSTRACT

Electrolyte composition can strongly affect the rate of crack growth in pipe steel X70. A weakly acidic citrate buffer (pH 5.5) and a mixture of NS4 solution with a borate buffer (pH 7) were used as background solutions under static and cyclic strain, respectively. Various compounds that affect steel dissolution and hydrogen absorption rates were added to the solutions. Crack growth is accelerated in the presence of metal dissolution activators but hindered upon addition of a corrosion inhibitor. Hydrogen absorption promoters do not accelerate the crack growth at the corrosion potential.

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## 1. Introduction

Stress corrosion cracking (SCC) has been identified as one of the primary reasons for failures in high-pressure buried pipelines [1–3]. Currently, the form of SCC in pipe steel under pipeline operation conditions is primarily determined by the composition of the environment. In sufficiently concentrated carbonate electrolytes at a high pH, intergranular SCC is observed in a narrow range of potentials around the active–passive transition. High pH SCC in pipelines utilises an anodic dissolution-based mechanism [4–7]. In dilute electrolytes with near-neutral pH (pH 5–7.5), transgranular cracking occurs in pipe steel at the potential region of its active dissolution [1–3,8].

Cracks on the external sides of pipe appear under delaminated coatings [1–3]. The chemical composition of the under coating electrolyte is primarily determined by the composition of the soil electrolyte [9]; this composition may also depend on the steel corrosion rate, the vital activity of various bacteria under a delaminated coating, and other factors [10].

The soil water composition might be notably diverse; it might depend on such factors as the soil type, the pipeline depth, the season, and the vegetation. The primary components of ground electrolytes include sulphate, chloride, carbonate (bicarbonate), and nitrate anions, as well as calcium, magnesium, and alkaline metal cations [11]. Soil contains organic compounds, primarily humic acids with widely varying concentrations and compositions. The

vital activity products of sulphate-reducing bacteria include hydrogen sulphide, thionic acids, and other sulphur-containing compounds. Therefore, the list of substances that can initiate and/or accelerate SCC of pipeline steels is extensive.

Due to the complex composition of soil electrolytes, the components of these electrolytes must be classified based on how they affect the rates of the partial corrosion reactions that occur in cracks. Today, most researchers agree that SCC of pipeline steels in environments at near-neutral pH results from the synergistic effects of mechanical straining, local anodic dissolution (AD), and hydrogen absorption (HA) [8,12–27]. Therefore, studying the influence of corrosive agents that activate or inhibit AD and HA of the metal on pipeline steel SCC remains relevant.

Studies involving the effect of soil water components (primarily dissolved CO<sub>2</sub>, H<sub>2</sub>S, O<sub>2</sub>) on the stability of pipeline steel in the context of cracking are generalised in references [3,10,28]. In particular, increasing the CO<sub>2</sub> concentration [8,22,29–31] or the presence of H<sub>2</sub>S [32] in synthetic soil electrolytes accelerate crack growth significantly. However, the reasons for these effects have not been established unambiguously. It has been seen that increasing the CO<sub>2</sub> concentration in electrolytes increases the overall acidity (i.e., buffer capacity) and the bicarbonate ion content, possibly accelerating pipeline steel AD [24,29]. And adding H<sub>2</sub>S to electrolytes may accelerate both hydrogen absorption and metal dissolution. The data describing the effect of other soil electrolyte components on crack growth do not generally agree regarding the effect of these substances on partial corrosion reaction rates. Therefore, no systematic study describing the effects of corrosive agents on the transgranular SCC of pipeline steels has been performed, even though such studies are necessary to understand

\* Corresponding author. Tel./fax: +7 495 3349805.

E-mail address: [mar@ipc.rssi.ru](mailto:mar@ipc.rssi.ru) (A.I. Marshakov).

the mechanism of this process and to improve the diagnostic methods used to detect corrosion in pipelines.

The background electrolyte and mechanical stress values are highly important when studying of the effects of corrosive agents on the SCC process in pipeline steel. NS4 solution [8], after being purged with an inert gas containing 5% CO<sub>2</sub>, is frequently used as the working electrolyte while studying the near-neutral pH SCC of pipeline steel. However, cracks do not grow in NS4 solution under static loading, even when the yield strength of the metal has been exceeded near the crack tip [28]. Steels can only crack under cyclic loading in this corrosive environment. A mixture of NS4 and borate buffer can be used to avoid changes in the pH of the working electrolyte when corrosive components are added [24,33].

Obviously, a buffer solution with a simple chemical composition in which a corrosion crack grows in a transgranular mode at a rate comparable to the crack growth rates in soil electrolytes should be used as the background electrolyte. These requirements are met by using a citrate buffer at pH 5.5 [34]. In this solution, the kinetic diagram of pipe steel degradation, specifically, the dependence of the crack growth rate ( $V$ ) on the stress intensity factor ( $K$ ), has a typical shape: one region displays a weak dependence of  $V$  on  $K$  between certain critical values of stress intensity factors in the corrosive medium ( $K_{SCC}$ ) and in an inert medium ( $K_C$ ). The crack growth rate at the strains corresponding to the plateau of the kinetic diagram depends on the composition and potential of the medium [34].

This work explores the effect of corrosive compounds on the crack growth rate in X-70 pipeline steel in near-neutral pH environments under static and cyclic mechanical tensions.

## 2. Experimental procedure

The test material was X-70 pipeline steel. The yield strength of the material was 538 MPa, and its ultimate tensile strength was 622 MPa. The chemical composition of the steel is presented in Table 1.

Rectangular specimens (200 × 17 × 5 mm) were cut from a pipe (1420 OD × 18.7 wall mm, Khartsyzsk Pipe Plant Co., Ukraine) along its axial line. Fatigue cracks measuring approximately 8 mm in depth were grown in the specimens to serve as crack growth initiators during the corrosion experiments. The fatigue cracks were approximately 0.5 μm wide.

Specimens were fastened in three-electrode cells that were filled with the electrolyte under study. Two loading modes were used. For the citrate electrolyte, a constant tensile strain was applied to specimens. For the NS4 solution, a triangle waveform straining was used at a frequency of 0.01 Hz, and a stress  $R$ -ratio of 0.65 and 0.85 ( $R$  = minimum stress/maximum stress).

**Table 1**  
Chemical composition (wt%) of X-70 pipeline steel and 08 kp steel.

Element	X-70 steel	08 kp steel
C	0.1	0.05
Mn	1.6	0.38
Si	0.33	0.03
Cr	0.03	0.05
Nb	0.05	–
Cu	0.018	0.15
Mo	0.03	–
V	0.005	–
S	0.006	0.04
P	0.03	0.035
Al	0.035	0.16
Ti	0.01	–
Ni	–	0.09

The rate of crack growth was determined based on the dependence of resistance ( $R_t$ ) on the experimental time ( $\tau$ ) as follows:

$$V = \frac{L_0 \left( \frac{R_t}{R_0} - 1 \right)}{\tau} \quad (1)$$

where  $R_0$  is the initial sample resistance, and  $L_0$  is the initial crack length. The sample resistance was measured according to a four-wire scheme using a BSZ-100-002 microhmmeter (NIIEMP, Penza, Russia) with an accuracy of 10<sup>−8</sup> ohm.

The stress intensity factor at the crack tip was calculated according to [35] using the expression for beam specimens with a through-edge crack:

$$K = \frac{P}{t\sqrt{b}} \left[ \sqrt{\frac{1}{\left(1 - \frac{L}{b}\right)^3 b}} \cdot \left( 1.941 - 1.741 \left(\frac{L}{b}\right) + 4.07 \left(\frac{L}{b}\right)^2 - 2.528 \left(\frac{L}{b}\right)^3 \right) \right] \quad (2)$$

where  $P$  is the load applied to the specimen,  $L$  is the crack length, and  $b$  and  $t$  are the specimen width and thickness, respectively.

The electrochemical measurements were carried out in a Devanathan–Stachurski cell using foil membranes (08 kp steel) measuring 100 μm in thickness with a work area of 3 cm<sup>2</sup>. The chemical composition of 08 kp steel is presented in Table 1. The membrane preparation technique and the experimental procedure are described in [36–37]. The potentiodynamic (1 mV/s) polarization curves were recorded from −0.8 to −0.3 V<sub>SHE</sub> using an IPC-Pro-MF potentiostat (Cronas Ltd., Moscow, Russia). The electrode potentials were measured with respect to the saturated silver chloride electrode and recalculated to use the standard hydrogen scale. A Pt plate was used as counter electrode.

The background electrolytes had the following compositions:

- citrate buffer solution (0.1 M C<sub>6</sub>H<sub>8</sub>O<sub>7</sub> + 0.25 M NaOH + 0.1 M KCl), pH 5.5;
- a mixture of NS4 solution and borate buffer solution with pH 7.0 (0.4 M H<sub>3</sub>BO<sub>3</sub> + 0.01 M Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>). The composition of the NS4 solution is presented in Table 2.

Additives (Table 3 and 4) were introduced as aqueous solutions. All solutions were prepared from reagent grade chemicals supplied by Labtex Ltd., Russia.

To identify the microstructure and crack propagation type (trans- or intergranular), metallographic sections were etched for 10–15 s in a 4 wt% solution of HNO<sub>3</sub> in ethanol. The micrographs were obtained with a NEOPHOT 2 microscope (Carl Zeiss, Germany).

## 3. Results and discussion

### 3.1. Effects of the corrosive components in the soil electrolyte and corrosion inhibitors on rates of iron anodic dissolution and hydrogen permeation into the metal

#### 3.1.1. Citrate buffer solution with additives

Fig. 1 presents the polarization curves, as well as plots of the current for hydrogen penetration through a membrane ( $i_p$ ) vs. potential in the background electrolyte and in the presence of 10 mM Na<sub>2</sub>S. Evidently, adding sulphide (S<sup>2−</sup> ions in the pH 5.5 solutions form hydrogen sulphide molecules and bisulphide ions) accelerates

**Table 2**  
Chemical composition (g/l) of the NS4 solution [8].

KCl	NaHCO <sub>3</sub>	CaCl <sub>2</sub> ·2H <sub>2</sub> O	MgSO <sub>4</sub> ·7H <sub>2</sub> O
0.122	0.483	0.181	0.131

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