Monitoring of mechanisms of formation of corrosive aggressiveness of soils and grounds of underground gas pipeline routes and on its basis assessment of service life of gas pipes in various soil-climatic zones

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Abstract. The experience of studying the problem of corrosive aggressiveness of soils and grounds in terms of improving the reliability of Gazprom's pipeline systems operation is summarized and presented. Soil factors causing surface corrosion of gas pipelines in soil conditions are studied. Based on the obtained results, it was suggested to evaluate not only the corrosive aggressiveness of soils and the gas pipe lifetime, but also the corrosive resistance of pipe metal in corrosive environments. Special attention is paid to the stress corrosion cracking formation mechanism.

1. Introduction
Corrosion aggressiveness of soils and grounds is currently a topical problem in modern gas pipeline construction and operation. Metal corrosion in underground conditions is the main reason for wear and tear of gas transportation systems. The actual service life of pipelines is determined primarily by the rate of metal corrosion. For steel pipelines built in 60-80s of the XX century, the standard service life was determined by 33 years [1]. By now, this design term has come to an end, but the pipelines continue to operate. Therefore, monitoring of corrosion aggressiveness of soils and grounds, and on this basis working out of the technology reducing and preventing development of corrosion processes, is a reliable basis for prolongation of service life of the iron pipelines laid underground.

The problem of determining the corrosive aggressiveness of different soils and grounds in relation to gas pipe steel is an urgent scientific and technical task. The rate of metal corrosion in various soils and grounds differs by its magnitude in dozens and even hundreds of times. The idea of corrosion aggressiveness of soils and grounds and its determinants is necessary when solving issues related to the development of technology to extend the life of gas pipelines, forecasting the sections of the highest corrosion rate, identifying the causes of stress corrosion cracking (SCC), justification of the method of pipe protection, etc. At the same time, it is important to have a quantitative characteristic of corrosive aggressiveness of soils and grounds in order to develop and apply technologies for the most reliable
protection of pipeline routes from corrosive destructive action. However, many criteria of an estimation of the corrosion aggressiveness connected with physical and chemical characteristics of soils and grounds, are reliable only within the limits of certain physical-geographical regions and their application in other regions is ineffective.

Relevance of this work is determined by the increased scale of economic and environmental disasters caused by the long-term operation of transcontinental gas pipelines, which is ultimately due to the lack of reliable methods to assess the interaction in the system "aggressive external environment of the containing thickness – pipeline". From the point of view of practice, it seems relevant to study the corrosive aggressiveness of each zonal soil and to develop on this basis the technology to reduce and prevent the corrosive aggressiveness of soils and grounds is not only an economic but also an environmental necessity.

2. Objects and methods
The objects of the study were the soils of the zonal series, including tundra, northern, middle and southern taiga, forest-steppe, steppe, dry steppe and semi-desert. Corrosion aggressiveness of zonal soils in relation to pipe metal was determined in the zonal series. In addition, the corrosion resistance of gas pipe metal in soils of the zonal series was determined. In laboratory conditions in soil samples determined the ionic composition of water extraction, particle size distribution, electrical conductivity, electrical resistance, hydrogen Clark Index, pH water in the soil sample with different degrees of moisture, magnetic susceptibility. Assessment of corrosive aggressiveness of the soil was determined by the most aggressive indicator.

3. Results and discussion

Types of corrosion aggressiveness of zonal soils
The introduction of a gas pipe into any zonal soil creates favorable conditions for the development of various types of corrosive aggressiveness. Hydrological, chemical, physicochemical, biological and other types of corrosive aggressiveness stand out among them.

3.1. Hydrological corrosive aggressiveness of soils
The initial mechanism of all types of corrosive activity in soils is the organization of a trench and laying of a gas pipe. Violation of soil integrity as a bio-inert matter of nature during trenching and gas pipe laying irreversibly changes soil properties and regimes. A special role in this is played by the natural process of constant saturation of the soil with the moisture of the near-pipe space. The pushing mechanism of soil saturation with water around the gas pipe is the gradient between the gas pipe temperature and the ground temperature. Condensation saturation of the water goes up to the full moisture content of the near-pipe soil. The moisture of the near-pipe soil is retained by capillary forces, forming anaerobic conditions for the development of anaerobic sulfate-reducing microorganisms. The presence of moisture in the soil has a significant impact on corrosion of pipe metal.

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Fe + H_2O = Fe(OH)_2
\]

Water is a component of soil electrolytes which interact with metal and create damage to gas pipes. We judge the qualitative composition of cations and anions of electrolytes by the water extract of each soil. The qualitative composition of the water extract determines the chemical aggressiveness of soils to the metal of the gas pipe.

3.2. Chemical corrosive aggressiveness of soils
The initial data on the assessment of the effect of water extract ions on metal corrosion were noted in the works [2-4]. It was found that the most aggressive are Cl⁻ and SO₄²⁻ ions. Their presence above 0.1% is an essential criterion of high corrosive aggressiveness of soil. First of all, chlorine and hydrogen ions destroy the protective film and thus accelerate the corrosion of metals. According to [5-8] the mechanism destroying the protective film is not clear. According to [1], the content of chlorine ions exceeds 0.1%, which causes greater corrosion of soils and natural waters in relation to steel. According to [9], the
The percentage of each anion from their sum characterizes its contribution to the overall acidic and alkaline corrosive aggressiveness of soils and grounds (table 1). By the sum of alkaline ions and each of them the coefficient of corrosive aggressiveness in grey forest soil reaches 0.6 and is characterized as increased. Corrosion aggressiveness as high on acid potential is noted in three samples.

**Table 1.** Anionic composition of water extraction of grey forest soils (Albic Luvisols).

| №  | Cl  | SO₄  | CO₃  | HCO₃  | Sum  | Coefficient Acid | Coefficient Alkaline | Corrosion aggressiveness by anion coefficient |
|----|-----|------|------|-------|------|------------------|----------------------|---------------------------------------------|
| 1  | 0.125 | 0.057 | 0 | 0.10 | 0.282 | 0.44 | 0.20 | 0 | 0.36 | Low |
| 2  | 0.120 | 0.343 | 0 | 0.68 | 1.143 | 0.11 | 0.30 | 0 | 0.59 | High |
| 3  | 0.125 | 0.042 | 0 | 0.05 | 0.217 | 0.58 | 0.19 | 0 | 0.23 | High |
| 4  | 0.125 | 0.393 | 0 | 0.75 | 1.268 | 0.09 | 0.31 | 0 | 0.59 | High |
| 5  | 0.125 | 0.111 | 0 | 0.35 | 0.586 | 0.21 | 0.19 | 0 | 0.60 | High |

Analyzing the ion composition of the water extract, it can be unequivocally said that each ion of the water hood in the interaction with water forms corrosive conditions with respect to the metal gas pipe.

Soil saturation of near-pipe space with water to the category close to the total porosity is the initial mechanism for the development of corrosive physical and chemical processes (table 2).
3.3. Physicochemical corrosive aggressiveness of soils

Physicochemical corrosiveness in soils and grounds is determined by redox processes called oxidation-reduction potential (ORP). In the zonal series, each soil type is characterized by a certain ORP value. In sod-podzolic soils, the ORP value varies from 550 to 750 mv. In chernozem ORP varies from 400 to 600 mv, and in serozems it varies from 350 to 450 mv [10]. Introduction of a gas pipe into the soil changes the character of water and temperature regimes, density, aeration, water permeability and other properties that lead to changes in ORP, pH, Clark Index and other properties. By the example of grey forest soil, it is shown that measurement of ORP in 5 samples in 10 replicates of grey forest soil indicates

### Table 2. Corrosion aggressiveness of soils.

| Type of water regime | Soils of the tundra and arctic areas of the polar belt | Soils of the steppe areas of the subboreal belt | Soils of semi-desert and desert areas |
|----------------------|------------------------------------------------------|------------------------------------------------|---------------------------------------|
|                      | Ground temperature, °C | Duration vegetative period with \( t > 0 \)°C, month | Moisture, % | pH water (80-120 cm) | Electrical resistivity, Ohm-m | rH2 | Pipe stability coefficient | Gas pipe lifetime, years |
| Auto-morphic          | Arctic tundra          | 32-44                                              | 5.8       | <20                  | >28                           | 1.6-1.8 | 64-72                     |
|                      | Tundra soddy           | 34-44                                              | 5.6       | <20                  | >28                           | 1.7-1.9 | 68-76                     |
|                      | Tundra soddy gley      | 42                                                  | 6.4       | <20                  | >28                           | 1.6-1.7 | 64-68                     |
|                      | Tundra peaty and peat-gley | 42                                                      | 6.2       | <20                  | >28                           | 1.7-1.9 | 68-76                     |
|                      | Boggy tundra           | 42                                                  | 6.4       | <20                  | >28                           | 1.9-2.2 | 76-88                     |
|                      | Alluvial soddy tundra  | 22-32                                               | 6.2       | <20                  | >28                           | 1.4-1.6 | 56-64                     |
|                      | Alluvial boggy tundra  | 20-26                                               | 6.0       | <20                  | >28                           | 1.6-1.8 | 64-72                     |
|                      | Chernozems             | <24                                                 | 6.5-7.0   | <20                  | <28                           | 1.0     | 40                        |
|                      | Brown semi-desert      | <32                                                 | 7.6-8.1   | <20                  | >28                           | 0.7-0.8 | 28-32                     |
|                      | Grey-brown semi-desert | <32                                                 | 7.7-7.8   | <20                  | >28                           | 0.7-0.8 | 28-32                     |
|                      | Solonetz semi-desert   | <32                                                 | 9.6-10.6  | <20                  | >28                           | 0.6-0.7 | 24-28                     |
|                      | Solonchaks semi-desert | <32                                                 | 9.8-10.7  | <20                  | >28                           | 0.5-0.6 | 20-24                     |
the development of gley process near-tube space in soils, at which ORP value was below 200 mv (table 3).

**Table 3. Oxidation-reduction potential (ORP) values (mv).**

| Sample number | Replicates |
|---------------|------------|
| 1             | 180 140 165 170 230 160 110 115 90 120 |
| 2             | 80 90 100 110 130 95 90 75 110 130 |
| 3             | 120 130 80 90 115 110 110 130 100 110 |
| 4             | 130 140 90 110 120 100 115 120 90 80 |
| 5             | 100 100 120 130 110 140 150 90 90 100 |

According to the assessment scale, the corrosive aggressiveness of the near-pipe space soil is characterized as strong and in some places average.

**Assessment scale of aggressiveness of ORP (mv) in soils:**

- Negative values: Very high
- Under 100: Strong
- From 100 to 200: Mean
- From 200 to 400: Weak
- Above 400: Non-corrosive

The concentration of hydrogen potential in the near-tube grey forest soil was calculated based on ORP and pH (acidic or alkaline values). At rather low ORP values rH2 did not exceed 23–25 units, which characterizes grey forest soil near-tube conditions as corrosive. It was found out that each zonal soil is characterized with different combination of corrosive-aggressive processes. It is very characteristic that combination of processes in each zonal soil changes depending on change of temperature or hydrological factor in seasonal cycle.

For example, let us give an example of complex development of corrosive-aggressive influence of grey forest soil on metal of gas pipe. Analysis of factors determining corrosive aggressiveness of soils shows that the most indicative integral factor characterizing corrosive aggressiveness of soils and grounds is the redox potential of soils and grounds. The main mechanism of ORP dynamics is change of trench ground watering in seasonal cycle.

On the one hand, anaerobic conditions contribute to the development of ORP, which itself as a process, dramatically increases the corrosive aggressiveness of soils and grounds, involving in the physical and chemical processes iron pipe itself. On the other hand, ORP characterizes aerobic and anaerobic conditions in soils. In this regard, the recovery regime can be judged on the development and vital activity of anaerobic sulfate-reducing bacteria. Sulfate-reducing bacteria under anaerobic conditions restore sulfates to hydrogen sulfate and sulphuric acid, which interact with iron, while emitting atomic hydrogen, which is stored in the structure of the metal pipe. The development of sulfate-reducing bacteria in soils requires strictly defined environmental conditions. The most important physiological feature of sulfate-reducing bacteria is their ability to develop under strictly anaerobic (complete absence of oxygen, oxides and oxygen-containing ions) conditions.

The analysis of the soil on which the pipe lies is very indicative in this respect. It is a dove-colored gleyed loam, whose ORP varies in the range from -80 to -96 mv at five measuring points. Low ORP values of the loam mean a high degree of its corrosive aggressiveness, which manifests itself in the pipe section with broken insulation tape.

The chemical composition of the protective crust above the corrosion cavity in the metal of the pipe taken under the broken insulation film included biological corrosion products, including oxides of divalent iron (FeO), hydroxides of iron Fe(OH)₂, iron sulphide (FeS), mineral siderite (FeCO₃). At
selection of samples hydrogen sulfide (H₂S) has been defined. Under the protective film the depression was located along the pipe. The width of the cavity was from 1.6 to 2.3 mm. In the head part of the cavity, in terms of gas movement in the pipe, the cavity width increased to 2.9-3.4 mm. The length of the cavity was 2.4 cm. The interaction of hydrogen sulfide with iron in the pipe forms iron sulphide and two hydrogen atoms. This process is called hydrogenation (saturation of pipe metal with atomic hydrogen), which dramatically reduces the corrosion resistance of pipes and their service life, leads to the development of SCC. Determination of gas pipelines trench corrosion aggressiveness by various methods allows to monitor corrosion activity of soils and grounds and on this basis to estimate service life of gas pipelines in different zonal climatic conditions and in different geochemical crust of weathering due to modern warming tendency.

The stated above shows that the problem of assessment of corrosion aggressiveness to metals of natural factors participating in underground corrosion of pipelines in Russia is a multifactorial system. In such a system, the initial mechanism in the development of metal corrosion is the condensation process of moisture accumulation in the near-pipe space. Saturation of near-pipe space with water leads to the development of anaerobic conditions as a medium for sulfate-reducing bacteria.

First of all, this complexity is connected with the fact that the rate of deep corrosion of pipes is predetermined not only by natural factors, but also by the state of insulation coating of pipes and operating modes of electrochemical protection stations.

According to numerous physicochemical data of soils and grounds very often in soils with the same physicochemical indicators, different rates of deep corrosion are revealed. Such facts can be explained only by different efficiency of electrochemical protection. Only a few pits can be distinguished from the total number of samples, where high rates of deep corrosion of metal and low values of protective potential are observed. These are the most representative sections of pipeline natural-technical systems for determining corrosion aggressiveness to metals of soils and grounds. The aforesaid allows to assume, that estimation of corrosion aggressiveness to metals of soils and grounds on speed of deep corrosion of metal of pipes in the conditions of work of stations of electrochemical protection is not quite correct. The complexity of corrosion processes lies in the fact that a single corrosion process runs simultaneously on anode and cathode. At the anode section, metal atoms are oxidized, i.e. electrons are emitted and transformed into ionic state, while at the cathode section ions (hydrogen, oxygen, iron) involved in the corrosion process are restored.

Secondly, the difficulty of determining the corrosion aggressiveness to metals of soils and grounds by the rate of deep corrosion is due to the inaccuracy of determining the rate of deep corrosion itself. For exact determination of the deep corrosion rate it is necessary to have 15–20-year monitoring (3–4 scientific field stations in each natural observation zone with the interval of 5 years).

Thirdly, the task of determining corrosion activity of soils is complicated by insufficient development of electrochemical theory of corrosion as applied to underground conditions. Corrosion products, formed in underground conditions and in conditions of cathode protection stations in operation, are poorly investigated. Many issues related to depolarization on cathode and anode pipeline sections are under discussion. The electrochemical theory of corrosion aggressiveness to metals of soils and grounds in the permafrost zone is especially poorly grounded. It is necessary to notice, that around pipes with "warm gas" in frozen soils a halo of thawing is formed and, in these conditions, (in the near-pipe space) electrochemical corrosion can occur on the usual (more southern) scheme. It is more difficult to estimate corrosion aggressiveness of frozen ground for pipes with "cold gas" (gas condensate or any other product).

In the literature there is an opinion that chemical reactions in the Far North are extremely slowed down due to weak water dissociation at low temperatures. The work of recent years has convincingly proved that perennially frozen soils of the permafrost zone are not a chemical rest zone and there are active processes of chemical and biological weathering, neoplasm and migration of substances. The main factors of the redox reaction in the permafrost zone are: unfrozen water, hydrogen ions and atomic oxygen. Dissolved gases, ions of salts and acids are concentrated in the film water. Chemical reactions in film water do not fade even at low temperatures. According to [11], even at low temperatures of soils
from 0 to -50°C the energy of redox processes increases. Therefore, it is possible to assume that potential corrosion activity of soils and grounds of the permafrost zone, despite high specific electrical resistance, is much higher than that of soils and grounds of the chernozem zone. In this connection it is possible to consider as rather debatable record in GOST (Russian National Standard) No. R 51164-98, paragraph 3.6: "Main gas pipelines, which wall temperature is lower than 268 K (-5°C), are not subject to electrochemical protection...". These questions are not theoretically grounded and require further research, theoretical and experimental substantiation. According to our observations, when the soil freezes, water in the soil solution passes from liquid to solid, to the form of ice. Decrease of dissolving volume of water in soil solution at ice formation is accompanied by increase of concentration of soil solution, thus chemical reactions of interaction of ions of soil solution with pipe metal in such conditions develop according to laws of reactions in saturated solutions.

4. Conclusions
The obtained materials allow making a number of general conclusions about the mechanism of corrosive aggressiveness of soils in relation to gas pipe metal in different soil-climatic zones. On their basis in the future it is possible to carry out an in-depth analysis of corrosive aggressiveness to metals of soils and grounds by geographical zones in the rank of groups of natural boundaries. On the other hand, this aggressiveness is realized in soils and grounds in relation to metal in conditions of broken pipe insulation. In this case, we must pay attention to the corrosion resistance of the gas pipe metal. In the zonal series of soils, we take chernozem soil as the soil standard, where the corrosion resistance of the gas pipe metal is taken as a unit, and the accident-free service life of the metal gas pipe is taken for 40 years under the condition of undisturbed insulation, the absence of factory cracks on the gas pipe and the quality of the weld.

Table 2 shows the data on corrosive aggressiveness of zonal soils by physical and chemical parameters. To the south from the chernozem zone soils of alkaline crust of weathering are formed. In alkaline soils the pH value of water extraction is more than 7.0. Such soils have high corrosive aggressiveness, therefore in them low corrosive resistance of pipe metal in relation to chernozem does not exceed 0.5–0.8 (table 2).

In alkaline conditions, the organ-iron film is soluble. Besides in soils with pH of water extraction above 8.2 there is carbonate ion $\text{CO}_3^{2-}$ which at interaction with sodium ion forms sodium carbonate, very strong corrosion destroyer of metal. This dramatically reduces the accident-free service life of the gas pipe, which is 24–32 years at soil temperatures near the pipe above 10°C and undisturbed insulation.

$$2\text{Na}^+ + \text{CO}_3^{2-} = \text{Na}_2\text{CO}_3$$

To the north of the chernozem zone, acidic crust soils of weathering are formed. Laboratory studies showed that organic matters play important role in soil aggressiveness. When fragment of gas pipe was placed in suspension of tundra zone soils organo-iron film was formed on the surface of sample. This film was the area where corrosive tundra soil and pipe metal surface were divided. In acidic environment organo-iron film is stable. Besides, in soils of circum-pipe space of Arctic and Antarctic regions the temperature does not exceed the first biological minimum (5.0°C), in conditions of which corrosive aggressiveness of chemical, physicochemical and biological processes sharply decreases, that promotes increase of accident-free service life of gas pipe in 1.4–2.2 times in comparison with chernozem (table 2). Based on the results obtained, it can be concluded that the service life of gas pipes in corrosive soils of alkaline and acidic weathering crusts can be extended, relative to the service life of gas pipes in chernozems, 2–4 times, if the gas temperature does not exceed the temperature of the first biological minimum – 5°C. At such temperature corrosion aggressiveness of biological, chemical and physical-chemical processes is sharply suppressed. Therefore, we recommend pumping gas through the pipe at a temperature no higher than 5°C, which will lead to the extension of accident-free operation of gas pipes.

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