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# **Corrosion problem in oil transportation**

Practical work

Physico-chemical basics and training technologies of hydrocarbons transport and storage

# 1. Corrosion problem in oil transportation

One of the most important factors in the service reliability decrease of internal pipeline metal surface is the impact of transported hydrocarbons containing active – corrosive components.

Annually, there are more than 70 thousand pipeline breakdowns and failures in Russia, of which 90 % are the results of corrosion damage. This includes 55 % in the gathering system and 35 % in lines of communication for formation pressure maintenance. More than 8 thousand km. of pipes, i.e. approximately 400...500 thousand tonnes of steel are used to replace these damaged pipes.

However, pipes of the same grade and diameter, identical microstructure and chemical composition and under similar operating conditions, significantly differ in their fail-safety term service: long-term operation without any damages and short-term with breakdowns and failures as a result of corrosion penetration.

According to research data in pipeline breakdown rate available from north Bashkir (table 1), more than 42 % of the pipes do not endure the 5-year service, while 17 % even a 2-year service due to pitting or crevice corrosion (fig. 1, and 2).

Table 1

r ipenne enardetensties					
Oil field	Total extension length (km)	Oil gathering line, %	Hydraulic line from pump station to trunk pipeline, %	Parallel pipelines, %	Conduit, %

Pipeline characteristics

Vategansk Uzhno-Jagunsk	1800	36	14	6	44
Arlansk					





Fig. 1. Research data of pipeline breakdown in north Bashkir



Fig. 2. Pipeline sample showing pitting corrosion

### 1.1. Basic terms and definitions

**Corrosion** is deterioration of intrinsic properties in a material due to reactions with its environment (oxidation of metals reacting with water or oxygen).

**Corrosion rate**  $K_m$  – a measure of the speed at which the metal grams is damaged per year on  $1m^2$  of area  $(gr/m^2 x hrs)$  or depth of process occurrence – distribution  $(mm \setminus year)$ .

$$K_m = \frac{m_0 - m_1}{S \times \tau},\tag{1}$$

where  $m_o$  – initial metal mass before testing, gr;

 $m_1$  – metal mass after testing, gr.;

- S operating sample surface,  $m^2$ ,
- $\tau$  testing period, hrs.

**Corrosion penetration** – (depth factor  $\boldsymbol{\Pi}$ , mm\year) is determined as:

$$\Pi = \frac{K}{\rho} \times 10^{-3},\tag{2}$$

where  $\rho$  – metal density, gr/cm<sup>3</sup>;

4

K – corrosion rate – gr ( $m^2$  per year).

One major factor determining the anomaly high corrosion rate is that fact there are specific non-metal inclusions in the steel which are of a corpuscular oxygen source and, in its turn, determines the rate of cathodic reactions on the metal surface.

**Classification according to deterioration**\_includes external corrosion (atmosphere and soil) and internal.

The main types of external surface corrosion is pitting corrosion, and internal corrosion – uniform or general corrosion due to oxidation-reduction heterogeneous processes occurring on the boundary phase surface.

Corrosion is also classified according to its formation characteristics, damage area, corrosion rate, and corrosion damage types (Fig. 3).

*Corrosion according to formation characteristics. Chemical corrosion* occurs in those environments where there is no electrical current. This is *external atmospheric corrosion*. Such corrosion is the result of the following two factors:

• *ferrum oxidation through oxygen* 

$$Fe^{+2(+3)} + O_2 = FeO \text{ or } Fe_2O_3.$$
 (3)

• *interaction of acid and alkaline environments, resulting in uniform films on the pipeline surface.* 



Fig. 3. Corrosion Classification

The destructive impact of atmospheric corrosion is insignificant and can be eliminated through enamel coatings and, simply, painting.

**Electro-chemical corrosion:** steel corrosion occurs in water environment as a result of electro-chemical reactions as current flow between separate surface areas (anodes and cathodes).

Metal reaction in the electro-chemical processes is determined as standard electrode potential value ( $E^{\circ}$ ). Several elements according to  $E^{\circ}$  are within the tension series which characterize their activity:

#### K, Ca, Mg, Al, Mn, Zn, Fe, H, Cu,

Every metal displaces from water solutions other metal salts, which are in the right side of this metal tension series.

The corrosion process is as following: on the anodes – oxidation:

$$Fe - 2e \rightarrow Fe^{2+}$$
 (4)

Iron atoms are as hydrated cathodes  $Fe^{2+}$  in the solution, i.e. anode metal *dissolution* occurs and corrosion penetrates deep into the metal.

The corrosion process on the cathodes is *reduction*:

$$2H^+ + 2e \to 2H_{ads}.$$
 (5)

Oxygen molecule ionization occurs forming hydroxyl ion in dependence to environmental pH: if pH < 4.3, then molecular hydrogen forms  $H + H \rightarrow$  $H_2\uparrow$ ; if pH > 4.3, resulting in the electron and oxygen reaction, dissolved in water, forming active hydroxyl groups:

$$O_2 + 2H_2O + 4 e \rightarrow 4 OH^-.$$
(6)

Further, cathodes  $Fe^{2+}$  and ions  $2OH^{-}$  react in the formation of ferrous oxide (Fig. 4):

$$Fe^{2+} + 2OH^{-} \rightarrow Fe(OH)_{2}.$$
 (7)

If there is a sufficient amount of free oxygen in the water, then ferrous oxide oxidizes to ferrous hydroxide as precipitation:

$$4Fe(OH)_2 + O_2 + 2H_2O \rightarrow \checkmark 4Fe(OH)_3. \tag{8}$$

As a result of the electric current anode split (decomposition): metals particles as  $Fe^{2+}$  ions proceed to water or emulsion flow. During anode split (decomposition), different breakdowns – flaws, caverns and others- occur.



Fig. 4. Electrochemical corrosion

*Classification according to deterioration* (Fig. 5) includes the following types:

- 1. *Uniform or general corrosion* which proceeds at approximately the same rate over the whole surface being corroded: iron rust, silver dulling.
- 2. *Isolated (local) corrosion* proceeds over single surface areas and include the following types:
  - spot- damage depth penetration is rather small and proceeds over a relatively significant surface area;
  - pitch deep penetration over small surface areas (D- length and h – corroded surface area are approximately the same);
  - *point (pitting) corroded surface area smaller than corroded pitch surface area (h > D.*

- 3. *Selective corrosion* dissolution of a single or several alloy components, resulting in porous residuum which retains its initial form and appears to be undamaged.
- 4. *Intercrystalline (intergranular) corrosion* results in corrosion at or near the grain boundaries of the metal. Corrosion proceeds immediately and deep resulting in catastrophic damages.
- 5. *Transcrystalline corrosion* is the most significant and dangerous corrosion type as it is not only near or at the grain boundaries, but also throughout the grain itself.
- 6. *Environment-induced corrosion* results from the joint action of mechanical stresses and corrosive environment. This corrosion is caused by hydrogen absorption formed during corrosion.



Fig. 5. Classification according to deterioration

It should be mentioned that special attention is paid to those questions connected with the transportation of oil (a rather aggressive fluid including not only hydrocarbon components, but also water, mechanical impurities, salts, free oxygen, aggressive hydrogen sulphide and carbon gases) and the internal pipeline corrosion research. To reveal internal corrosion conditions it is necessary to design specific prevention requirements for premature pipeline breakdown failures.

# 1.2. Specific Features of Internal Pipeline Corrosion in West-Siberia



The analysis of the factors that influence internal pipeline corrosion are as following:

- localized corrosion breakdowns of the lower pipeline section and emergency failures are evident when oil watering increases to 50 %, oil emulsions are unstable and water is evolved as a separate phase;
- weak corrosive formation (reservoir) water: mineralization of calcium chloride water is insignificant and includes 20 ... 40 gr/litre, pH water is neutral, temperature 40 °C;
- oil emulsion in the water phase contains up to 250 mgr\l dioxide carbon and 2...10 mgr/l hydrogen sulphide;

- associated oil gases include up to 6%  $CO_2$  and 1.5 mgr  $\mbox{m}^3$  hydrogen sulphide;
- West Siberian oil is paraffin, light and low-viscous, with insignificant stability of oil emulsion.

It has been noted that *salt fallout in the water phase of well production* is a characteristic feature in West Siberia and that metal corrosion occurs as *carbon process*. Calcium carbonate  $CaCO_3$  deposition (fallout) occurs on the internal pipeline surface. In several cases, pipeline coating can sag due to  $CaCO_3$  deposition. This could occur as a result of either mechanical factors such as abrasive impact of suspended particles, hydraulic impact, pipe vibration due to gas plugs or mechanic-chemical coating dilution of those sections under significant stress conditions.

Exposed metal section, as well as, the pipeline surface covered by a precipitation forms *galvanic macrobed*, where the metal is anode, and the pipeline surface- cathode. Intensive corrosion occurs at a rate of 5...8 mm per year.

High anomaly corrosion rate (5...8 mm per year) is the electrode area ratio: small anode area in the lower pipeline section as paths, while cathode area is ten times more than the electrode anode one.

## **1.3.** Factors influencing internal pipeline corrosion

**Temperature and pH water impact** The intensity corrosion behavior dependence to pH and temperature is illustrated in Fig. 6. The following analysis shows three major dependence zones to pH value:

- *pH* < 4.3 (strong acid environment)- corrosion rate significantly increases at pH decrease;
- $4.3 < pH < 9 \dots 10 corrosion$  rate insignificantly depends on pH;
- 9-10< pH < 13 (strong alkaline environment) corrosion rate decreases at pH increase and corrosion practically ceases at the value of 13.

**Temperature rise** increases anode and cathode processes (corrosion rate) due to the rate increase of ion movement.

**Oxygen content in water** Dissolved oxygen in water is a significant factor influencing corrosion and alters above-mentioned dependence (Fig. 7). As mentioned above, pipes are exposed to intensive corrosion in acid environment at pH < 4.3 and practically no corrosion at pH > 4.3, if there is no dissolved oxygen in the water (Fig. 7, curve 4). If there is dissolved oxygen in the water, then iron corrosion occurs not only in an acid but also alkaline environment (Fig. 7, curves 1...3).



Fig. 6. Intensity corrosion behavior dependence to pH and water temperature



Fig. 7. Intensity corrosion dependence to oxygen content in water

**Fractional pressure CO**<sub>2</sub> **impact** A significant impact on metal corrosion damage is free carbon (CO<sub>2</sub>) in formation water. Under identical pH *corrosion in a carbon environment is more significant than in strong acid solutions*.

According to research data, pipeline systems at  $P_{CO2} \le 0,02$  mPascals - uncorrosive; at  $0,2 \ge P_{CO2} > 0,02$ -probably average corrosion rate, while at  $P_{CO2} > 0,2$  mPascals – high-corrosive environment.

The  $CO_2$  impact on corrosion environment intensity is connected with  $CO_2$  content- forms in water solutions:

- dissolved gas CO<sub>2</sub>;
- non-dissociated H<sub>2</sub>CO<sub>3</sub> molecules;
- biocarbonate HCO<sub>3</sub> ions;
- carbonate  $CO_3^{2-}$  ions.

Under equilibrium conditions there is a balance between all abovementioned forms:

$$CO_2 + H_2O \Leftrightarrow H_2CO_3 \Leftrightarrow H^+ + HCO_3^- \Leftrightarrow 2H^+ + CO_3^{2-}.$$
 (9)

 $CO_2$  impact can be explained as:

- *CO*<sub>2</sub> content leads to the increase of hydrogen isolation at cathode;
- *carbonate-oxide film formation on the metal surface*

H<sub>2</sub>CO<sub>3</sub> molecules spontaneously react in the cathode process:

$$H_2CO_3 + e \rightarrow H_{a\partial c} + HCO_3^{-} \tag{10}$$

Cathode reduction is exposed to bio-carbonate ions:

$$2HCO_3^- + 2e \to H_2 \uparrow + CO_3^{2-}. \tag{11}$$

 $H_2CO_3$  is an absorber and supplies required hydrogen ion  $H^+$  in cathode reaction:

$$H_2CO_3 \iff H^+ + HCO_3^-$$
 (12)

The interaction of  $\text{Fe}^{2+}$  and  $\text{HCO}_3^-$  or  $\text{H}_2\text{CO}_3$  form ferrum carbonate precipitation FeCO<sub>3</sub>:

$$Fe^{2^+} + HCO_3^- \rightarrow FeCO_3 + H^+$$
(13)

$$Fe^{2+} + H_2CO_3 \to FeCO_3 + 2H^+ \tag{14}$$

It was noted that corrosion product-iron significantly influences corrosion rate:

$$4FeCO_3 + O_2 \rightarrow 2Fe_2O_3 + 4CO_2 \uparrow \tag{15}$$

These precipitations are semi-pervious for corrosive- aggressive environment components and slow down metal deterioration. Thus, two specific features of carbon dioxide can be distinguished:

- 1. hydrogen isolation increase on the cathode
- 2. oxide carbonate film formation on the metal surface.

Water mineralization impact Dissolved salt in water is electyles, in which case, their concentration increase up to a definite limit increases the environment electro-conductivity and, as a result, accelerates corrosion.

Moreover, corrosion rate decrease is associated with the following items when mineralization increases:

- decreases dissolution of gases CO<sub>2</sub> and O<sub>2</sub> in water;
- water viscosity increases, leading to such troubles as diffusion, oxygen admission to pipeline surface ( to cathode areas).

**Pressure** rise increases not only  $CO_2$  dissolution, but also salt hydrolysis.

#### Hydrodynamic parameters -

at low transporting fluid velocity, water-oil emulsion sagging occurs with further formation of water sublayer and mechanical impurity transport and their precipitation on pipeline walls (stagnant zones).

Index of hydrodynamic water-oil emulsion flow regime types is **Froude** number:

$$Fr = \frac{V^2}{Dg},\tag{16}$$

where *V*-mixture flow velocity, m sec.

*D* – *internal pipe diameter, m* 

*g* - acceleration of gravity,  $m \setminus sec$ .

At  $\mathbf{Fr} < 0.2$  emulsion exfoliation occurs and corrosion develops at the low pipeline section. At  $\mathbf{Fr}$  from 0.5 to 2.25 oil -emulsion is formed in the water (corrosion damage is high); at  $\mathbf{Fr} > 2.25$  – water-emulsion type in oil (corrosion rate sharply decreases).

Under conditions of rather low flow velocity (0.1...0.9 m/sec) structure exfoliation of rxc develops, i. e. water is isolated (evolved) into a separate phase. Oil-emulsion and gas will be flowing above the water.

Waves develop on the interface boundaries due to the viscosity difference of two adjacent phases. As these waves advance along the transporting fluid flow a secondary effect at the interface occurs: water droplet detachment and its rotation (Fig. 8). This causes the formation of *eddy paths* composed of numerous water droplets along the *lower generatrix of pipeline*.



Fig. 8. Eddy wave formation on the oil-water interface surface

Those mechanical impurities (carbonate and sulphide ferrum, sand and clay) in the water phase are partially ingressed in the rotating water droplets and participate in the constant *hydro-erosion impact* in the lower pipeline section.

**Flow pattern** Relative phase flow velocity (gas and fluid) in liquidgas mixtures (LGM) including their physical properties (density, viscosity, surface tension, etc.), sizes and location in the pipeline determines the formation of two-phase (multi-phase) flow patterns. There are seven major patterns (Fig. 9): bubble, plug, gravitational, wavy, gas-piston, annular and dispersed. Each of the above-mentioned flow patterns influences corrosion process. The high-lightening question is the interaction of corrosion in the pipeline to flow patterns and the transporting liquid-gas mixtures. However, this information is insufficient in solving the problem of corrosion.

It is known that annular (dispersed-annular) flow decreases pipeline corrosion intensity, while gas-piston (plug-dispersed) flow stimulates pipeline corrosion-erosion failure in the lower generatrix of pipeline at elevated pipeline route sections.

Gravitational (smooth gravitational) – develops uniform (general) and pitting corrosion in lower generatrix of pipeline sections, as well as, in the so-called liquid "traps" especially, salt water release into a *separate* phase.



Fig. 9. Liquid-gas flow patterns in horizontal pipes

**Bio-corrosion** produced by the exposure to micro-organisms (Fig. 10), i.e. sulphate- regenerating anaerobe bacteria (reduction of sulphate to sulphide) which can be found in waste (sewage) water, oil wells and pay zones.

As a result of sulphate-reduction  $H_2S$  (hydrogen sulphide) is formed, which in its turn, dissolves in oil, further reacting with iron and forming sulfide ferrum as precipitation:

$$Fe + H_2 S \rightarrow FeS \downarrow + H_2 \uparrow$$
. (17)

 $H_2S$  affects the wettability of the metal surface and this surface becomes hydrophilic, i.e. water-wet, and a thin electrolyte film is formed on the pipeline surface where sulfide ferrum (FeS) accumulates.

Sulfide ferrum (FeS) is a corrosion agent as it participates in galvanicmacrobed formation  $\rightarrow$  Fe – FeS, which in its turn, is cathode; and where only metal Fe as anode will be destroyed.



Fig. 10. Metal bio-corrosion

**Chlorine calcium water** also affects corrosion. Chlorine ions activates with metal due to the fact that chlorine ions have a high absorbability on metals. Chlorine –ions displace (expel) inhibitors from the metal surface, promoting inhibitor film dissolution and simplifies metal ion conversion into the solution. Chlorine ions significantly affect the dissolution of ferrum, chromium, nickel, aluminum and others.

### Pipeline protection from internal corrosion

The main prevention methods (Fig. 11).in internal surface corrosion are the following:

- *different technological measures;*
- corrosion inhibitors;
- *high-effective and economic coatings (polymer, silicate, metal and combined coatings);*
- corrosion-resistant pipes and non-metallic materials (Fig. 12).

The most effective anti-corrosion protection is inhibitors as such inhibitors hamper corrosion crack formations on the metal surface. Besides, many inhibitors penetrate into the developing crack apex and withhold corrosion development. Thus, one important factor is the appropriate choice of an inhibitor so that such inhibitors not only slow down corrosion uniformly and locally, but also effectively suppress corrosion initiation and further development of corrosion-failure cracks.



Fig. 11. Pipeline protection form internal corrosion



Fig. 12. Glass-fiber pipe with metallic coating

Another highly effective coating is thermal treatment of pipes. However, thermal treatment regime should be chosen in accordance to corrosive environments and corrosion behavior for each specific field. This, in its turn, requires additional research.

### **Corrosion inhibitors**

**Corrosion inhibitors** an additive of organic or inorganic origin, used to retard undesirable corrosive actions. Inhibitors are surface- active substances.

To significantly increase pipe reliability, durability and safety, appropriate inhibitor protection for internal metal pipe surfaces is necessary. (Fig. 13).

Behavior mechanism of inhibitors is as following: polar inhibitor molecules are absorbed on the internal pipe surface forming a film to protect this surface from water contact. Thus, one condition for electro-chemical reaction is excluded: hydrogen ion discharge does not occur due to the protective film and metal dissolution is slowed down. Such inhibitors are termed as cathode inhibitors, as they affect the reaction rate on the anode. There are also anode inhibitors which affect the reaction on the anode.



Fig. 13. Pipe samples without inhibitor application: a) oil pipeline b) highpressure conduit

The selection of this or that inhibitor depends on watering. At watering of up to 30 %, inhibitors dissolved in water phase are preferable.

Film-forming inhibitors are more effective when the water content increases in oil.

Efficiency of corrosion inhibitors depends on many factors, one of which is how the inhibitor having attained the protected metal surface and is being absorbed. Low inhibitor concentration can increase corrosion instead of decreasing it.

Multi-phase flow conditions complicate the selection of appropriate corrosion inhibitors. Inhibition should be initiated before the formation of corrosion on pipeline walls. On elevated sections channeling corrosion occurs more frequently due to abrasive removal of inhibitor film along the lower generatrix of pipeline, thus the desirable protection effect can not be attained.

Being a rather expensive pipeline corrosion protection, it demands exact technological requirements. The selection of an inhibitor for specific conditions involves additional information as costs, research results, and development testings, which according to *GOST 9.506-87 is determined by the protecting inhibitor index properties- corrosion and protection rate* (Fig. 14).



Fig. 14. Steel samples: a) treatment with inhibitors; b) without inhibitors

Inhibitor efficiency is determined in accordance to GOST 9.506-87:

$$Z = \frac{K_1 - K_2}{K_1} 100, \tag{18}$$

or inhibition coefficient:

$$\alpha = \frac{K_1}{K_2},\tag{19}$$

where  $K_1$  and  $K_2$  – corrosion rate with  $\setminus$  without inhibitors.

### Example of unit for corrosion inhibitor

Different dosage chemical agent units are applied to introduce corrosion inhibitors into the oil gathering and treatment system (Fig. 15, 16). The following dosage chemical agent unit «Ozna Dozator» designed by Ozna Co. Ltd. (Oktjabtsk, Bashkortostan Republic) will be described further.



Fig. 15. Dosage chemical agent unit "Ozna Batcher"



Fig. 16. General view of dosage chemical agent unit "Ozna Batcher" in a heated room

Dosage unit is to introduce liquid demulsifying agents and corrosion inhibitors into the trunk pipeline system for oil demulsification inside the pipeline, as well as, pipeline equipment corrosion protection. Specification for dosage chemical agent unit (DCAU) «Ozna Dozator» is described in table 1.

Table 1

<b>Characteristics</b>	Values
Power supply – current type	variable three-phase
Voltage, watt	380
Frequency, Herz	50
Kinematic viscosity of dosage environment,	0,00085
$m^2$ /sec, not more	
Continuous operation time, hrs.	up to 960
Temperature of chemical agent dosage, °C	from 20 to 60
Environment temperature, °C	from -40 to +40

## Specifications

### Dosage chemical agent unit (DCAU) includes:

- dosage pump continuous volume dosage for liquid demulsifying agents and corrosion inhibitors;
- wheel pump infilling of chemical agents into reservoir and periodic mixing of the chemical agent;
- daily service welded rectangular cross-section reservoir dosage of specified volume of liquid demulsifying agents and corrosion inhibitors in the pipeline for a required time period;
- welded rectangular cross-section reservoir heating and storage of chemical agents with installed electric-heater. Reservoir is connected to liquid measurement unit to visually control the liquid level.

### Technological steps in injecting corrosion inhibitors

There are several technological methods in applying corrosion inhibitors:

- continuous dosage
- continuous dosage with preliminary intensive dosage;
- *plug method;*
- *periodic discharge;*
- formation injection.

Four types of corrosion inhibitors were tested in Arlansk oil field (Vjatsk area), applying various methods (table 2).

# Table 2

	Economic results mil roubles Protection impact, %					
Suggested method	Record-608	XPK- 002B*	Sonkor- 9801	Azimut 14 B		
<b>Constant dosage in</b> oil gathering system and trunk pipeline	-	2,957	1,670	1,584		
απά πατικ ριρετιπε	10,1	61,8				
			66,3	70,8		
<b>Periodic dosage</b> in every two weeks during two days	18,298	17,909	18,078	18,089		
	10,1	61,8	66,3	70,8		
Periodic dosage + magnetic treatment	15,498	15,109	15,278	15,289		
	67,4	85,4	71,9	78,7		
<b>Constant dosage in</b> oil gathering system	10,595	8,542	9,213	9,257		
	10,1	61,8	66,3	70,8		
Constantdosageonly in oil gatheringsystem +magnetic	7,795	5,742	6,413	6,457		
treatment	67,4	85,4	71,9	78,7		

Comparative analysis of suggested method efficiency (corrosion inhibitors)

## 2. Task types

Iron corrosion involves the presence of oxygen, aggressive carbon dioxide and hydrogen sulphide in water.

In **formation** water there is equilibrium:

$$Ca^{2+} + 2HCO_3^{-} \leftrightarrow CaCO_3 + CO_2 + H_2O_.$$
(19)

According to this equilibrium equation, to sustain a definite bicarbonate – ion concentration  $HCO_3^-$ , there should be a corresponding amount of free  $CO_2$  concentration in water, which in its turn, is termed as **equilibrium**.

If the amount of  $CO_2$  in water is more than the equilibrium concentration, then this **redundancy** causes  $CaCO_3$  dissolution, i.e. the equilibrium is shifted (left) and water **pH** is increased to 3.5 when intensive metal corrosion begins. Such water is termed as **aggressive.** If there is  $CO_2$  deficiency in water in comparison to equilibrium, then bicarbonate – ion  $HCO_3^-$  concentration dissociates, i.e. the equilibrium is shifted (right) resulting in the release of carbonate calcium precipitation  $CaCO_3$  from water.

If the factual amount of carbon dioxide in water coincides with equilibrium concentration, then there is no carbonate calcium release from the water, which in its turn, can not dissolve  $CaCO_3$ . Such water is termed as **stable** (pH = 7).

### Task 1. Determine aggressive carbon dioxide in formation water and the water type.

Water type and the presence of carbon dioxide is determined in accordance to the chemical composition of water (table 3).

Table 3

Ion content, mgr \ l						Free CO <sub>2</sub> ,	
Na <sup>+</sup>	K	<i>Ca</i> <sup>2+</sup>	$Mg^{2+}$	СГ	<i>SO</i> <sub>4</sub> <sup>2-</sup>	HCO <sub>3</sub> -	mgr \ l
26,3	7	25,9	17	18	11,5	195,2	17,6

Mineralized water composition

#### Solution

1. Amount of aggressive carbon dioxide is determined in accordance to diagrams, designed by F.F. Laptev, based on the content of fixed and free carbon dioxide, which is:

$$\frac{rHCO_3^{-}}{rCa^{2+}},\tag{20}$$

where,  $r_1$  – ion content in the following equivalent.

$$r_i = \frac{q_i}{\beta_i}, \, \mathcal{M}\mathcal{Z} - \mathcal{H}\mathcal{K}\mathcal{B} / \mathcal{I}$$
(21)

where,  $q_1$  – ion content, mg/l;  $E_i$  –ion equivalent (Table 4);  $M_i$  – ion molecular mass;  $B_i$  – ion valency.

### Ion equivalents

Ion	$Na^+$	Mg <sup>2+</sup>	Ca <sup>2+</sup>	$\mathbf{K}^{+}$	Fe <sup>3+</sup>	Cl	<b>SO</b> <sub>4</sub> <sup>2-</sup>	HCO <sub>3</sub> <sup>-</sup>	CO <sub>3</sub> <sup>2-</sup>
$M_i$	23	24	40	39	56	35,5	96	61	60
$B_i$	23	12	20	39	18,6	35,5	48	61	30

Diagram  $\mathbb{N}_{2}$  1 (fig. 17) is applied in case 22, in all other cases- diagram  $\mathbb{N}_{2}$  2 (fig. 18).

$$1,25 > \frac{rHCO_3^{-}}{rCa^{2+}} > 0,75.$$
 (22)

In the following case, ratio value  $\frac{rHCO_3^-}{rCa^{2+}}$  is:

$$\left(\frac{195,2}{61}\right):\left(\frac{25,9}{20}\right) = 3,2:1,295 = 2,471,$$

as, obtained value is more than 1,25, then further calculations is based on diagram  $N_{2}$  2.

2. To arrive at this equation, we obtain the equivalent sum of  $Ca^{2+}(a)$  and  $HCO_3^{-}(b)$  and doubled free carbon dioxide CO2 content (c).

$$rCa^{2+} = a = 1,295 \text{ M2} - \Im \kappa B / \pi,$$
 (23)

$$rHCO_{3}^{-} = b = 3,2 \text{ M2} - \Im\kappa \beta / \pi,$$
 (24)

25

Table 4

$$rCO_2 = c = \frac{17.6}{44} = 0.4 \text{ M2} - 3\kappa \theta / \pi,$$
 (25)

$$a + 2c = 2,095,$$
  $b + 2c = 4,0.$  (26)

These sums are expressed as a point on the curve, corresponding to equivalent content of equilibrium  $HCO_3^- = 3.7 \text{ mgr} - \text{eq/l}$ .

In this case, water contains 3,2 mgr – eq/l HCO<sub>3</sub><sup>-</sup> (formula 24), i.e. equilibrium equivalent content HCO<sub>3</sub><sup>-</sup> is more than 0,5 mgr – eq/l (3,7 - 3,2 = 0,5). Thus, there is HCO<sub>3</sub><sup>-</sup> deficiency in respect to CO<sub>2</sub> in formation water. Otherwise, CO<sub>2</sub> redundancy imparts water corrosive activity.

3. According to diagram  $N_2$  2,  $HCO_3^-$  deficiency as 0.5 mgr –eq/l corresponds to  $CO_2$  redundancy as **11** mgr/l.

4. To determine water type according to Culin classification (table 5) six major equivalent ions are considered.

Table 5

Water type	Super-sulfated sodium	Hydro-carbonate sodium	Chlorine magnesia	Chlorine calcium
Ion content ratio	$(Na^{+}+K^{+})/CI^{-} > 1$	$(Na^{+}+K^{+})/CI^{-} > 1$	$(Na^{+}+K^{+})/Cl^{-} < 1$	$(Na^{+}+K^{+})/CI^{-} < 1$
	$(Na^{+}-CI^{-})/SO_{4}^{2} < 1$	$(Na^{+}-CI^{-})/SO_{4}^{2} > 1$	(Cl <sup>-</sup> -Na <sup>+</sup> )/Mg <sup>2+</sup> < 1	(CI <sup>-</sup> -Na <sup>+</sup> )/Mg <sup>2+</sup> >1

Culin classification of natural water



Fig. 17. Diagram № 1



Fig. 18. Diagram № 2

### Home task

**Task 1:** Water type is determined according to chemical water composition and the presence of aggressive carbon dioxide (table 6).

Table 6

			Ion	content,	mgr/l			Free CO <sub>2</sub> ,
Var.	Na <sup>+</sup>	$\mathbf{K}^+$	Ca <sup>2+</sup>	$Mg^{2+}$	Cľ	<b>SO</b> <sub>4</sub> <sup>2-</sup>	HCO <sub>3</sub> -	mgr/l
1	2	3	4	5	6	7	8	9
1	13,9	2,3	16,6	8,1	10,6	8,9	96,5	63,1
2	294	13,6	139	42,6	46	196	244	21,1
3	50,0	18,5	200	30	210	100	610	660
4	9,9	1,2	29,8	8,5	6,1	18,3	120	8,1
5	172	15,2	115	59,4	202	328	344	26,3
6	149	31	84,2	25,3	229,4	120	415	12,7
7	52,5	24,0	280,6	1,2	13,6	28,0	705	553
8	223	30,8	148	65,2	451,8	319	281	21,1
9	13,9	1,9	26,1	8,4	8,3	12	132	25,9
10	200	25,8	110	59,7	208	318	340	24,9
11	45,5	4,6	43,9	18,6	47,0	75,1	174	26,0
12	65	36	198,8	40	295	846	732,4	1320
13	13,2	3,2	16	7,9	10	9,1	95	64,1
14	299	17,0	137,6	44,0	45,9	196,9	240	20,9
15	51,2	16,9	199,6	31,2	218,3	98,9	600	654
16	10,1	1,4	28,6	9,2	7,0	17,9	125	8,7
17	178,0	14,2	121,3	58,5	204,3	326,6	347	26,0
18	155,0	32,4	83,2	26,1	224,6	118,3	405	12,0
19	51,1	26,8	279,6	1,4	12,9	26,9	697	558
20	227,3	31,2	151,2	64,6	439,2	321	290	20,1
21	12,9	1,87	26,6	8,2	8,1	14,2	138	26,0
22	204,0	25,1	112,3	58,6	206,2	311	339	24,4
23	45,1	4,0	41,8	19,4	49,2	74,8	184	2620
24	65,8	38,6	197,6	41	293,2	840	732,4	1310
25	170,0	18,2	124,3	54,0	209,0	320,6	338,2	27,2
26	150,0	38,1	80,2	24,9	226,6	120,3	409,2	13,0
27	50,1	26,2	279,3	1,89	13,9	27,2	696,9	552,4
28	209,0	20,1	119,3	56,6	209,2	318,3	326,3	21,9
29	180,0	15,0	122,6	54,5	202,0	326,6	347	25,8
30	150,0	34,3	80,2	24,3	221,2	110,1	411	15,6

# Input data

### Task 2: Evaluation of corrosion inhibitor efficiency

Determine application efficiency of corrosion inhibitor "Sonkor" at inhibition coefficient  $\alpha$ , 2 injections in pipeline gathering system: 1<sup>st</sup> – constant dosage of an inhibitor; 2<sup>nd</sup> – periodic dosage with magnetic treatment (table 7).

Table 7

Factor	Value
Sample area $S$ , $M^2$	0,15
Mass before experiment $m_1$ , gr	350
Mass after experiment, at constant dosage $m_2$ , gr	349,915
Periodic dosage + magnetic treatment $m_2'$ , gr	349,920
Experiment time at constant dosage $\tau$ , in 24 hours	7
Periodic dosage + magnetic treatment $\tau'$ , in 24 hours	5
Mass decrease of sample without water inhibitor, % in 24 hours	0,007

### Algorithm solutions

### Algorithm solutions

- 1. Calculate sample mass without inhibitor after 5 and 7 hours of experiment time.
- 2. Determine corrosion rate *K* of sample without inhibitor.
- 3. Determine corrosion rate K of sample with inhibitor at constant and periodic dosage in combination with magnetic treatment.
- 4. Calculate effective inhibitor under different injection conditions.

# VOCABULARY

RUSSIAN	ENGLISH
надежность	service reliability
система сбора	gathering system
условия эксплуатация	operation conditions
авария	breakdown \ failure
замена (труб)	replacement
сквозной коррозия	corrosion penetration
канавочная коррозия	crevice corrosion
язвенная коррозия	pitting corrosion
протяженность	extension length
нефтесборный провод	oil gathering line
напорный нефтепровод	hydraulic line
магистральный нефтепровод	trunk pipeline
водовод	conduit
внутриплощадочные	parallel pipelines
нефтепроводы	
коррозия	corrosion
разрушение	deterioration $\$ damage $\$ failure
действительный	intrinsic
скорость коррозии	corrosion rate
проникновение коррозии	corrosion penetration
включений	inclusion
атомарный	corpuscular
равномерная \ общая коррозия	uniform \ general corrosion
окислительно-	oxidation-reduction
восстановительный	
гетерогенный	heterogeneous
раздел фаз	boundary phase \ interface
точечная коррозия	pitch
структурно-избирательная	structural-selective
коррозия	
межкристаллитная коррозия	intergranular
коррозионное растрескивание	cracking

окисление	oxidation
химическая коррозия	chemical corrosion
местная коррозия	local corrosion
сплошная коррозия	uniform
атмосферная коррозия	atmospheric corrosion
почвенная коррозия	soil corrosion
биокоррозия	bio-corrosion
контактная коррозия	contact corrosion
среда	gas-phase corrosion
пятнами	spot (patchy)
пленка	film
покрытие	coating
напряжение	tension
вытеснять	to displace
растворение	dissolution
восстановление	reduction
осадка	precipitation
свищ	flaw
каверн	cavern
потускнение	dulling
ржавление	rust
повреждение	breakdown
сохранять	retain
абсорбция водорода	hydrogen absorption
агрессивный флюид	aggressive fluid
сероводород	hydrogen sulphide
свободный кислород	free oxygen
механические примеси	mechanical impurities
преждевременный	premature
аварийный порыв	emergency failure
обводненность	watering
пластовая вода	formation (reservoir) water
двуокись углеводород	dioxide carbon
попутные нефтяные газы	associated oil gases
выпадение	fallout

гальваническая макропара	galvanic macrobed
отслаиваться	sag
взвешенная частица	suspended particle
пробка	plug
протекание	behavior
сильнокислая среда	strong acid environment
сильнощелочная среда	strong alkaline environment
выделение	isolation
кислотность	acid
парциальное давление	fractional pressure
влияние	impact \ effect
равновесное условие	equilibrium condition
подвод	admission
гидролиз	hydrolysis
перекачиваемый	transporting
скорость течение	fluid velocity
застойная зона	stagnant zone
вихревая дорожка	eddy path
нижней образующей трубы	lower generatrix of pipeline
капель воды	water droplets
газожидкостная смесь	liquid-gas mixture
структурная форма потока	flow pattern
пузырьковая	foam (bubble)
снарядная	gas- piston
пробковая	plug
кольцевая	annular
расслоенная	gravitational
волновая	wavy
дисперсная	dispersed
сульфат	sulphate
сульфид	sulphide
сточная вода	waste (sewage) water
продуктивный горизонт	pay zone
сульфид железа	sulfide ferrum
смачиваемость	wettability

гидрофильный	hydrophilic,
стимулятор коррозии	corrosion agent
абсорбируемость	absorbability
пассиватор	inhibitor
дозирование	dosage
обработка	treatment
очистка труб	pigging
цикличность перекачки	swapping cycle
тормозить	to hamper
сдерживать	to suppress
зарождение коррозия	corrosion initiation
термообработка	thermal treatment
снижать	to retard
надежность	reliability
долговечность	durability
водовод	conduit
стендовое испытание	development testing
коэффициент торможения	inhibition coefficient
установка	unit
реагент	chemical agent
деэмульсация	demulsification
частота	frequency
напряжение	voltage
кинематическая вязкость	kinematic viscosity
заполнение	infilling
емкость	reservoir

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