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## Corrosion inhibitors – application in oil industry

The efficient flow of natural gas and oil to recipients is very often disrupted due to corrosion processes. They cause deterioration of material, leading to changes in their mechanical properties, such as durability, hardness or elasticity. In time, the progress of these phenomena causes damage to storage tanks or transmission systems which as a result, leads to leakage. Corrosion processes affect not only transmission and storage of fossils. The scale of the problem is much greater. Devices and systems corrode at the stage of exploration, production (corrosion of drilling equipment) and petroleum processing (corrosion of refinery plants). Currently, the opportunity to resolve the existing problems regarding corrosion, both for the domestic and global oil and gas industry is emerging. It is estimated that corrosion processes cost the American industry 280 billion dollars per year. Part of this sum is allocated to the oil and gas industry. Since this phenomenon cannot be stopped, more and more often the extent of damage to particular materials is being monitored. This solution seems to be economically justified. The article discusses mechanisms of the mentioned phenomenon, including also biocorrosion. Furthermore, some factors are presented which contribute to the occurrence of this unfavorable process in the oil industry. Additionally, some methods which decrease as well as prevent the effects of corrosion are discussed, with particular emphasis on corrosion inhibitors.

Key words: corrosion, biocorrosion, corrosion inhibitors.

### Inhibitory korozji – zastosowanie w przemyśle naftowym

Przepływ gazu ziemnego oraz ropy naftowej do odbiorców bardzo często ulega zakłóceniom, spowodowanym procesami korozji. Powodują one niszczenie materiału, polegające na zmianie jego właściwości mechanicznych, m.in. wytrzymałości, twardości czy sprężystości. Postępująca w czasie korozja przyczynia się do uszkodzenia zbiorników magazynujących czy instalacji przemysłowych, a w konsekwencji do wycieków danego surowca. Obecnie krajowy i światowy przemysł naftowy i gazowniczy stoi przed rozwiązaniem istniejących problemów związanych z tym zjawiskiem. Ponieważ nie da się zapobiec występowaniu korozji, coraz częściej podejmowane są działania kontrolujące stopień uszkodzenia danego materiału. Procesy korozji dotyczą nie tylko przesyłu i magazynowania wyżej wymienionych kopaliny. Skala tego zjawiska jest znacznie większa. Korodowaniu ulegają m.in. urządzenia i instalacje na etapie poszukiwania, eksploatacji (korozja urządzeń wiertniczych) oraz obróbki surowców (korozja instalacji rafineryjnych). Szacuje się, że procesy korozji kosztują amerykański przemysł 280 miliardów dolarów rocznie, z tego 1,4 miliarda dolarów pochłania sektor naftowy i gazowniczy. W artykule zostały omówione mechanizmy wyżej wymienionego zjawiska, z uwzględnieniem procesu biokorozji. Ponadto, przedstawiono czynniki, które przyczyniają się do występowania tego niekorzystnego procesu. Omówiono również sposoby łagodzenia i zapobiegania korozji, ze szczególnym uwzględnieniem zastosowania inhibitorów korozji.

Słowa kluczowe: korozja, biokorozja, inhibitory korozji.

### Introduction

Corrosion is an unbelievably demanding problem which the global and domestic industries have to solve. This issue is much more complex in the oil and gas sector. These phenomena are present at each stage, from the fossil exploitation [24], transportation and distribution to safe storage.

Also, fuel material refinement is affected by corrosion. The corrosion processes, including biocorrosion contribute to the deterioration of the mechanical properties of drilling platforms and equipment, storage tanks and refinery plants. Long-term damage to pipelines can lead to oil spills into the

environment. Thus causing local contamination of ground and water environments culminating in significant economical loss.

It is estimated that corrosion processes cost the American industry 280 billion dollars per year. According to United States Cost of Corrosion Study conducted by NACE International, US oil and gas exploration and production industry spends 1.4 billion dollars on corrosion. In detail, 0.6 billion dollars is attributed to surface pipeline and facilities cost, 0.5 billion dollars to downhole tubing and 0.3 billion dollars to capital expenditures related to corrosion [14]. Financial outlays in the amount of 1.372 billion dollars, which the industry spends every year to fight corrosion, present the scale of the phenomenon. Half of this sum, concerns the oil and gas industry, since corrosion is regarded as an especially important issue for this branch.

The range of this phenomenon depends mainly, on the type of raw materials and the environment in which it occurs. In case of oil tanks or pipelines, the scale of these processes is determined by the composition of the medium: type of oil (e.g. different sulfur content), the ratio of oil-water phases or water salinity. Oxygenated drilling fluid introduced at

the drilling stage is an excellent carrier of oxygen, a strong oxidant. Then, not only the borehole piping is exposed to corrosion, but also the drilling equipment, pipelines and tanks used for storing the fluid. Moreover, water or carbon dioxide pumped into the deposit creates an excellent environment for corrosion initiation.

Undesirable activity of microorganisms results in the occurrence of biocorrosion which deteriorates the properties of the used material. The biogenic processes appear at the stage of extraction, transportation and storage of the fossils mentioned. Currently, more and more significance is being attributed to sulfate-reducing bacteria (SRB). They contribute to the deterioration of gas quality (by generating H<sub>2</sub>S) and modification of the mechanical properties of particular materials [12].

Preventive steps and actions that hinder the occurrence of corrosion consist mainly of using active substances acting as inhibitors. There are many active substances which are components of corrosion inhibitors. Their presence in commercial preparations is varied. At present, some chemical compounds are being withdrawn from the market as their use possess a great toxicity risk.

### The mechanism of corrosion and biocorrosion

Electrochemical corrosion involves all the processes that take place when various electrochemical potentials arise on metal surfaces in an electrolyte environment. The electrochemical potentials generate the electrochemical (corrosion) cell, in which the surface of the metal with lower potential is the anode on which metal oxidation takes place. Whereas the metal surface with a higher potential becomes the cathode on which reduction processes take place. It can be observed as dissolving of the anode metal and it leaves a deposit of metal on the cathode. In the same way, the properties of a particular material (metal or alloy) are changing, which results in corrosion pits or reduces the metal's durability. Corrosion processes occur in the presence of:

- electrolyte (e.g. water solutions, humidity, etc.), which displays ionic conduction,
- metal, the surface of which is not homogeneous (the point of contact of various metals, lack of homogeneity in the crystalline structure of specific metals).

Steel, which apart from iron has a carbon additive (0.2%) in the form of iron carbide or graphite, is an example of a material which corrodes easily. The heterogeneity of the steel surface in the presence of electrolyte creates areas of different electrochemical potentials. Then, on the steel surface, electrochemical (corrosion) microcells are created, and anode (iron) and cathode (carbon) areas appear.

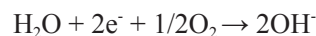
Positively charged iron ions Fe<sup>2+</sup> on the anode pass on to the solution, while free electrons (e<sup>-</sup>) move through the steel to the cathode, where, together with water and oxygen they create OH<sup>-</sup> ions. These ions pass through the electrolyte and react with iron ions creating the iron(II) hydroxide Fe(OH)<sub>2</sub>, which, due to further oxidation changes into rust. Below, is a diagram of oxidation-reduction reactions (figure 1), which occur on the positive and negative electrodes of the corrosion cell [22].

**Reactions occurring on the anode** – metal oxidation and its loss:

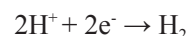


**Reactions occurring on the cathode**

- in neutral or alkaline environment the oxygen is the electron acceptor:



- in acid environment protons act as hydrogen acceptors:



The products of electrode reactions often come into secondary reactions and they form insoluble compounds which make tight layers like rust on the surface of iron alloys or patina on the surface of copper alloys.

Rust forms a deposit on the metal surface. This deposit consists of three non-compact layers with different oxidation states of iron in each of them. The deepest layer is mostly the greenish iron(II) hydroxide  $\text{Fe}(\text{OH})_2$ , another layer is black magnetite  $\text{Fe}_3\text{O}_4$ , whereas the external layer consists mainly of orange iron(III) hydroxide  $\text{Fe}(\text{OH})_3$  [4, 11, 29].

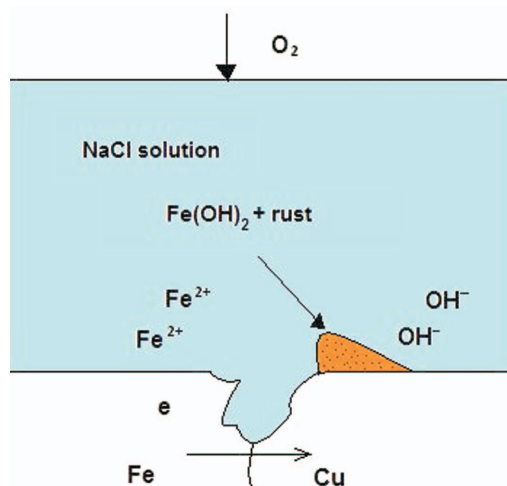


Fig. 1. Diagram of corrosion cell [22]

In cathode-anode reactions, oxygen and water are used. Water, which is necessary for continuing the process, is regenerated. Therefore, corrosion on dry surfaces or in dry systems does not occur. It probably does not exist either in the environment of relative humidity below 60%, whereas the optimal humidity required for the development of corrosion is 70–80%. Furthermore, corrosion is observed in systems completely immersed in water which contain dissolved oxygen.

Apart from galvanic corrosion there is also biocorrosion. **Biocorrosion** (MIC – *microbiologically influenced corrosion*) is the corrosion which arises due to the presence of microorganisms [28, 30]. It generally covers all the processes of damaging the original metal structure as a result of the direct presence of microorganisms or products of their metabolic activity. It is estimated that biocorrosion constitutes about 10% of metal corrosion as a whole. Moreover, it is considered that

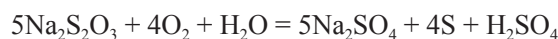
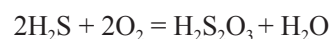
the oxidation factor in corrosion caused by microorganisms is higher than in the corrosion resulting from the effects of the atmosphere.

MIC may occur in strictly specified conditions which allow microorganisms to grow and multiply. The necessary and essential condition for microbes to multiply, is water. Effective activity of the water should remain at the level of over 0.9. Additionally, the growth and proliferation of microorganisms take place in the presence of electron donor, reduced electron acceptor, energy and carbon source.

Taking into account the conditions necessary for the process, two kinds of biocorrosion can be distinguished:

- aerobic,
- anaerobic.

Bacteria represented by *Acidithiobacillus* spp., e.g. *Acidithiobacillus thiooxidans* have the ability to oxidize both  $\text{Fe}^{2+}$  and sulphur compounds (e.g.  $\text{FeS}_2$  pyrite) in an acid environment (pH below 4) with low oxygen concentration:



*Gallionella* microaerophiles and representatives of: *Sphaerotilus*, *Crenothrix*, *Leptothrix* and *Clonothrix* participate in oxidation of iron oxide and forming typical bumps on the surfaces of corroded metal. The final product is the rust-coloured iron(III) hydroxide  $\text{Fe}(\text{OH})_3$  which results as an oxidation product of iron(II) hydroxide  $\text{Fe}(\text{OH})_2$ . It leaves a deposit in niches or joints of welded elements (gas and oil pipelines).

Apart from the described bacterial genera and species which cause biocorrosion, there is also *Pseudomonas* spp. It is a microorganism strongly engaged in corrosion processes occurring in industrial water. By creating bacterial consortia with other bacteria types, *Pseudomonas* spp. actively proliferate on the metal surface. Furthermore, it is possible for them to grow in slime because of reduced oxygen requirements

Table 1. Examples of bacteria responsible for induction of metal corrosion [2, 5, 8, 13, 20, 25]

Group of bacteria	Example of microorganisms	Corrosion mechanism
Oxidants of sulphur or sulphide	<i>Acidithiobacillus thiooxidans</i> , <i>Acidithiobacillus ferrooxidans</i>	Sulphuric acid production
Iron bacteria	<i>Gallionella</i>	$\text{Fe}^{2+}$ to $\text{Fe}^{3+}$ oxidation
Filamentous bacteria	<i>Sphaerotilus</i> , <i>Crenothrix</i> , <i>Leptothrix</i> , <i>Clonothrix</i> , <i>Pedomicrobium</i>	$\text{Mn}^{2+}$ to $\text{Mn}^{4+}$ oxidation
Manganese bacteria	<i>Metalogenicum</i> , <i>Leptothrix</i>	Cathodic depolarization
Hydrogen-using bacteria	<i>Clostridium</i> , <i>Desulfovibrio</i>	Hydrogen ionization
Hydrogen-producing bacteria	<i>Clostridium which reduces sulphates</i>	Cathodic depolarization
Thermophilic bacteria	<i>Thermodesulfobacterium thermophilum</i>	$\text{Fe}^{3+}$ reduction to $\text{Fe}^{2+}$ ions
Biofilm-creating bacteria	<i>Pseudomonas</i> spp.	Creating a biofilm or slime

in relation to aerophilic bacteria. Therefore, they use the remnant oxygen which is present in the system and create an anoxic environment. It generates favorable conditions for the development of anaerobic sulfate reducing bacteria (SRB).

Sulfate reducing bacteria mostly participate in the process of anaerobic bacteria induced corrosion, initiating the corrosion of steel elements of containers or technical systems. It is estimated that nearly 77% of corrosion in American extraction boreholes is related to SRB.

It is mostly SRB that are associated with biocorrosion and dissolution of metal surfaces [10, 12, 15]. They are characterized by their capability to transmit hydrogen to sulfate(VI), sulfate(IV) and thiosulfate as the final electron acceptors. In this way these compounds are reduced to sulfides. SRB can use hydrogen and thus they take part in the cathodic depolarization of the metal surface.

Examination of the MIC processes, in which SRB took part, enabled to determine factors in which redox processes occur most intensively. Namely, in the presence of iron and under changeable aerobic and anaerobic conditions, corrosion of metal is accelerated. It is assumed that temporary oxygenation activates sulfate reducing bacteria and the remaining bacteria which live in an anaerobic population on the metal surface. In the process, a strongly acidic environment arises

(as a result of the presence of metabolism of acidic products, e.g. acetates), responsible for metal corrosion. A visible mark of corrosion caused by SRB is the black deposit of iron(II) sulfide FeS on the metal surface. The removal of this deposit reveals the anode hollows of pure iron which yields to rapid corrosion and causes significant damage. The mechanism of corrosion induced by SRB is particularly complex. Below, are reactions which may potentially occur:

- Anode reaction:



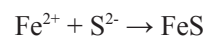
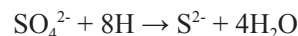
- Water disintegration:



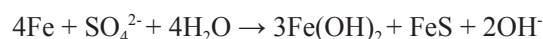
- Cathodic reaction:



- Reactions with SRB bacteria:



- Summary reaction:



### Corrosion and biocorrosion in oil and gas industry

Corrosion and biocorrosion are exceptionally extended issues which cannot be ignored when discussing the problems of damage to the materials used in the oil and gas industry [14, 17, 26]. The scale of the mentioned processes is huge and concerns practically all oil industry branches. These processes occur in:

- extraction of fuel sources (both natural gas and oil). There are also secondary and tertiary methods of oil deposit intensification, which are connected with additional acidification, of the deposit environment. These activities contribute further to the spread of corrosion and biocorrosion [3],
- transmission and storage,
- refinery processes.

The corrosion which occurs inside transmission systems or storage tanks depends on the temperature, CO<sub>2</sub> content, H<sub>2</sub>S, water presence, the flow velocity of specific fluids and condition of the steel surface which the system or tank is made of. Most pipelines are made of steel with carbon additive which makes it prone to corrosion. Currently, there is a tendency to replace the alloy named above with materials more resistant to corrosion. Unfortunately, this solution increases the costs of production.

The attempt to classify the processes which take place

in the oil industry is extremely problematic and ambiguous. Of course, various division criteria can be selected, e.g. interaction mechanism, the area of industry which is affected most by corrosion, observed changes or the preventive measures undertaken. However, no matter what criteria are adopted, they are unable to embrace the magnitude or scale of this phenomenon. Taking into account the mechanisms of corrosion, the following corrosion types should be singled out: electrochemical, chemical and mechanical. The electrochemical type has been already described above. Whereas the chemical and mechanical corrosions will be discussed shortly.

Chemical corrosion occurs when metal surface corrodes under the influence of strong oxidants (atmospheric oxygen, sulfur and hydrogen sulfide). Unlike electrochemical corrosion, the chemical type is not accompanied by the flow of electric current.

The processes of the discussed corrosion are associated with the presence of the following elements in the system [32]:

- elementary sulfur, polysulfides and hydrogen sulfide,
- CO<sub>2</sub>,
- O<sub>2</sub>,
- strong acids (e.g. Cl<sup>-</sup>, F<sup>-</sup>),
- concentrated brines.



Carbon dioxide is one of the most aggressive factors which stimulate corrosion. It dissolves in water and creates carbon(IV) acid  $H_2CO_3$ , leading to pH reduction in the environment. Corrosion induced by carbon dioxide is hindered by e.g. temperature and pH changes (pH shift towards alkaline environment). The rise in temperature makes the deposits of iron carbide settle on the metal surface and the protective layer which ensues hindering of the corrosion process. Corrosion is stimulated by carbon dioxide and enhanced by the presence of oxygen and organic acids. They dissolve the passive metal layer and prevent further sedimentation of iron(II) carbide. The appearance of carbonates in the environment increases pH, which hinders corrosion. Acetates also modify the process of damage done to the metal surface; the lower the acetate concentration, the less effective the corrosion.

Apart from  $CO_2$ , oxygen also quickly reacts with metals as a very reactive oxidant. Oxygen, dissolved in oilfield water, is the basic and very often the main source of corrosion in devices, borehole machines and transmission systems (oil and gas pipelines).  $O_2$ , which acts as an electron acceptor, leads to corrosion of the anode metal. Additionally, its presence in the environment accelerates corrosion caused by  $H_2S$  and  $CO_2$ .

Strong acids (HCl, HF) are very often used in stimulation treatments by pumping the treatment fluid into the borehole in order to increase the permeability of the area near the borehole. In the case of calcareous rock, usually the 5÷28% HCl solution is used. Therefore, ions  $Cl^-$  acting as donors, are present. Oxygen and low pH accelerate the attack of  $Cl^-$  ions on the metal surface. In addition, temperature,  $Cl^-$  concentration and metal stress, influence the metal surface corrosion. Chloride ions are extremely aggressive factors which destroy the protective metal layer when interacting with it. This results in depassivation and exposes the metal surface to more rapid corrosion. Similarly as corrosion induced by oxygen, the one caused by chlorides affects the pipelines.

Elementary sulfur, which is often a deposit fluid component, it is a very strong oxidant. It also takes part in the corrosion process. However, the mechanism of corrosion caused by elementary sulfur remains unexplained. Acidification of the environment which contains elementary sulfur occurs in the presence of  $H_2S$ ,  $H_2SO_4$ ,  $H_2SO_3$  and  $H_2SO_2$  in such systems. According to MacDonald et al. hypothesis [16], electrochemical reactions between these substances and the iron are the power which drives corrosion processes. The effect of these reactions is the appearance of appropriate iron sulfides  $FeS_x$ .

Moreover, we can distinguish:

- microbiologically induced corrosion (MIC),
- galvanic corrosion,
- erosion corrosion,
- crevice corrosion.

Worth mentioning is also galvanic corrosion. This type of corrosion occurs when two metals of different electrochemical potentials come into contact with each other, and they are in an electrolyte solution. The result is an electrochemical cell. This type of corrosion is most common between stainless steel and carbon in anaerobic environment.

In turn erosion corrosion arises on almost every type of metal and material. It causes mechanical removal of the metal's protective layer, due to fast flow of fluids. The erosion of this layer accelerates corrosion. Factors determining the occurrence of this phenomenon are: the rate of fluid (medium) flow, the amount of solid particles suspended in the medium (e.g. sand), morphology and density of particles. Most probably, this process is connected with corrosion caused by  $CO_2$ .

Biocorrosion also affects the oil and gas industry. Microorganisms existing in a particular environment (pipeline or tank) have the tendency to accumulate in the form of bio-film on a specific surface, creating favorable conditions for corrosion initiation (environment acidification). At present, environment protection makes it essential to recognize the corrosion mechanisms and work out preventive methods.

The hazard of harmful substance leakage into the environment can bring disastrous effects to the natural environment and potential accidents for the population. This issue is particularly vital in the case of extensive transmission systems of oil and natural gas. That is the reason why models are developed concerning:

- simulation of corrosion mechanisms in hydrocarbon transmission systems,
- conditions necessary for initiation of processes,
- the occurrence of damage in steel,
- predictions of potentially hazardous situations, on the basis of collected technical data.

In addition, preventive measures are introduced in order to reduce the risk of transmission failure caused by corrosion.

The parameters mentioned in literature in mathematical models take into account the results of experimental studies and contribute to the explanation of corrosion and biocorrosion. They bring us closer to the issues which concern material durability in oil and natural gas transmission systems [6].

### Corrosion inhibitors

Corrosion inhibitor is a chemical agent whose task is to hinder the process of damage to the material. It creates

a tight protective film on the surface of the material (metal) or facilitates the metal's passivation. The inhibitors hinder

corrosion but do not remove the changes formed earlier i.e. rust, slime etc. In general, organic and inorganic compounds are used as corrosion inhibitors. Considering the mechanism of action, inhibitors can be divided into: anodic, cathodic and mixed cathodic-anodic. The effectiveness of these inhibitors largely depends on the pH of the environment. Some of them demonstrate good protective properties exclusively in neutral solutions, whereas in acid electrolyte they do not affect the range of corrosion and sometimes even promote it. There are also compounds which are active only in acid environment. Most inhibitors affect specifically one metal or a group of metals, but they do not provide protection to a greater number of metals or alloys. The exception are chromates which passivate most of the metals [4, 11, 27].

Taking into account the mechanism of action, the following can be singled out:

- **inhibitors which create protective layers**

This group comprises of organic compounds which are adsorbed on the surface of the corroding metal, creating in this way a tight protective film. The extent of adsorption of the compound determines the corrosion rate, reducing it considerably when the metal is completely isolated from the corrosive environment.

Another method of creating a protective layer is passivation, which is based on chemical interaction of the surface of the corroding metal with a potential inhibitor. In this way, the metal surface is covered with an insoluble protective layer whose main components are oxides. This group of compounds comprises e.g. organic phosphates and chromates.

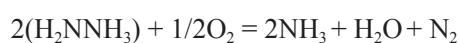
- **inhibitors which neutralize the environment**

These compounds, represented by amines or ammonia, reduce the concentration of  $H^+$  ions in the environment. However, these type of inhibitors are not very popular in the oil industry.

- **scavengers**

Another method to inhibit or totally eliminate corrosion is the application of substances which will remove the corrosion initiators from the environment.

Hydrazine and sodium sulfate(IV) demonstrate this type of action, as they bond the molecules of oxygen and eliminate it from the environment. At present, they are the most commonly used inhibitors of the scavenger type.



- **others**

Apart from using inhibitors, another method of protection from corrosion or biocorrosion is the application of metal coating (insulating and shielding films), inorganic (enamel, oxide, phosphate and chromate films) or organic (paints,

lubricants, oils, polymers), as well as electro-chemical (anodic or cathodic) protection.

### **Anodic inhibitors**

The inhibitors, discussed below, block the course of the anodic process. They are usually anions which create insoluble compounds in the anodic areas with the ions of dissolved metal. This group includes redox substances, the so-called passivators (e.g. chromates, dichromates, nitrites) and compounds which form insoluble films (e.g. phosphates, benzoates – acting only in the presence of oxygen). The mentioned anodic inhibitors are very effective, however they may show unfavorable action. Inhibitors acting as oxidizers, reduce themselves so their concentration in the solution diminishes. Too low concentration of the inhibitor accelerates the corrosion, therefore only a few anodic areas are protected. Thus in practice, higher inhibitor concentration is used than the one theoretically indispensable.

### **Cathodic inhibitors**

Cathodic inhibitors inhibit the cathodic process through:

- reduction of oxygen concentration in the solution,
- increase in the overpotential of hydrogen liberation.

The first group comprises of cations  $Mg^{2+}$ ,  $Ca^{2+}$ ,  $Zn^{2+}$  which bind the oxygen and precipitate as hydroxides, sulphates or carbonates, creating a protective film in cathodic areas. Hydrazine and sodium sulphate(IV) also known as cathodic inhibitors.

The second class of cathodic inhibitors are represented by bismuth ( $Bi^{3+}$ ) and arsenic ( $As^{3+}$ ) ions which increase the overpotential of hydrogen liberation.

In comparison with anodic inhibitors, any concentration of applied cathodic inhibitor leads to a noticeable decrease in corrosion rate, which is an undeniable asset of this type of solution. However, much lower effectiveness and efficiency of corrosion inhibition when compared with anodic inhibitors are the drawbacks of such a solution. In conclusion, to make an appropriate and rational choice, all positive and negative aspects of specific methods need to be considered.

### **Anodic-cathodic (mixed) inhibitors**

Anodic-cathodic inhibitors are substances which moderate both the anodic and cathodic processes simultaneously. Organic compounds containing N or S (e.g.: amines, thiols, organic sulphides) are considered to possess such activity. This class of agents adsorb in an active centre on the metal surface, such interaction is associated with the van der Waals bonds and electrostatic forces (physical adsorption). However, chemisorption is regarded as a key factor in the case of the most effective inhibitors.

In general, the success of organic inhibitors depends on the extent of the covering on the metal surface. Maximal protection is usually achieved by monomolecular film. The higher the inhibitor concentration, the greater the protection of the metal surface, until the maximum value is achieved. Once the value

is achieved, the protection decreases. In many cases, when the inhibitor concentration is too high, the corrosion acceleration is observed (above the maximum value). The cause of this relation should be sought in the arising soluble complexes of inhibitor and metal or cathodic reduction of the inhibitor's molecules.

### The application of corrosion and biocorrosion inhibitors in industry

Substances considered as potential corrosion inhibitors, should be characterized by the following physical and chemical properties:

- durability,
- inability to precipitate in the form of residue,
- inability to form emulsion.

Corrosion inhibitor, potentially applied in the oil industry, should possess sufficient solubility in hydrocarbons.

The selection of an appropriate corrosion inhibitor intended for specific industrial applications is an extremely complex issue [19]. The effectiveness of a specific agent, among other things, depends on:

- the type of material which interacts with the inhibitor,
- the aggressiveness of the environment (e.g. pH of the environment, the presence of redox substances),
- the place where the inhibitor is applied (refinery, gas and oil pipelines, drilling equipment, etc.). This is absolutely vital as in each environment there are various compounds which induce corrosion and microorganisms which induce biocorrosion. There is nothing like one universal set of corrosion inhibitors that can be applied both in the borehole and technical installation,
- the type of transferred or stored fuel.

Furthermore, the factors which determine the selection of a specific application is the toxicity of the proposed agent, harmlessness towards the environment and profitability of the chosen option.

As already stated, there are a few anti-corrosion methods, including:

- rational selection of appropriate material (metal, alloy) intended for specific application. That selection should take into account the type of medium the metal will be in contact with (natural gas, fuel, petroleum), the type of equipment or installation where it will be used (transmission installations, storage tanks, drilling equipment) and other factors.
- reduction of aggressiveness of the environment; this method involves introducing a neutralizer, for example ammonia, caustic soda, sodium carbonate or low molecular weight amines.

In the oil industry, during the processing of sulfurous oil, the facilities for fractional distillation are particularly prone

to corrosion. Distilled oil is highly aggressive because of the presence of:

- hydrogen sulfide (dissolved or as a product of pyrolysis of sulfur compounds),
- hydrogen chloride (originating from magnesium and calcium chlorides from deposit waters),
- carbon dioxide dissolved in oil,
- oxygen dissolved in oil,
- naphthenic acids,
- oilfield water (which occurs together with oil and creates electrolyte).

Fractional distillation plants are built mainly of carbon steel. However, in the most corrosion vulnerable condensation-cooling systems of atmospheric towers, copper alloys are used. They are more corrosion resistant than carbon steel.

In most cases, the equipment used in drilling is exposed to corrosion induced by the presence of oxygen, carbon dioxide and hydrogen sulfide [23]. Out of all these compounds, it is the carbon dioxide that is the most common factor to induce corrosion, while hydrogen sulphide is the most hazardous compound which poses threat not only to human life but also to the environment.

As mentioned before, corrosion and biocorrosion are extremely important as they directly reflect specific economic loss [3, 7, 9]. Research work is being conducted on new potential corrosion inhibitors and modification of the existing ones, in order to effectively eliminate from the endangered system, the factors responsible for corrosion. The application of chemical agents with desired properties is absolutely necessary as they allow to avoid further damage in refinery plants or tanks [18, 19].

Based on the chemical nature, corrosion inhibitors may be placed into one of the following groups:

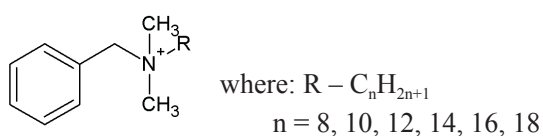
- amines and ammonium salts,
- imidazoline,
- quaternary ammonium salts,
- heterocyclic compounds which possess a nitrogen atom.

In common applications, the oil and gas industry prefers to use hydrophobic corrosion inhibitors. Taking into account their physical and chemical properties they are more effective as they ensure that an additional permanent protective layer is created on the surface of the metal.

The corrosion inhibitors used currently are multicomponent mixtures. The concentration of the active component is between 30÷40%, the remaining fraction is the hydrophobic solvent (e.g. petroleum) [31].

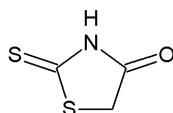
Sometimes corrosion inhibitors should demonstrate hydrophilic properties. In this case, surface active agents or active polar compounds (e.g. quaternary ammonium salts) are added to the mixture. Below, some chemical compounds, commonly applied in oil and gas industry, are presented. Their inhibition capabilities were also discussed.

**Benzalkonium chloride** (alkyldimethylbenzylammonium chloride) is a quaternary amine which acts as a surface active agent. Additionally, it is used as a corrosion inhibitor, cationic surfactant and phase separation factor in the chemical industry.



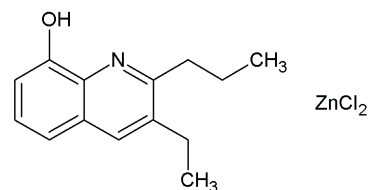
benzalkonium chloride

An example of a commonly used corrosion inhibitor is rhodanine (2-thioxo-4-thiazolidinone) and its derivatives (3' – and 5' –) [34]. They are used as corrosion inhibitors of iron to protect petroleum refinery plants.



rhodanine

Another group of modern compounds that may be used as corrosion inhibitors are complexes with zinc (Zn) or cerium (Ce). The complex of 2-propyl-3-ethyl-8-oxychinolin with  $ZnCl_2$  [33] was successfully used as a corrosion inhibitor on steel surfaces in an environment rich in  $O_2$ . This compound is obtained in condensation reaction between of  $ZnCl_2$ , *o*-aminophenol and aldehyde in benzene presence.



2-propyl-3-ethyl-8-oxychinolin –  $ZnCl_2$

Generally, corrosion inhibitors in the oil industry are added to fracturing fluids. Apart from active substances, corrosion inhibitors also contain alcohols used as components preventing the precipitation of iron and carbonates (table 2).

These data were included in a compilation [21] of the year 2011. Despite certain toxicity, the chemical agents prevent the action of compounds, which are even more hazardous to humans and the environment such as hydrogen sulfide, reduce the contamination by microorganisms and prevent uncontrolled proliferation of bacteria. Moreover, these substances eliminate the risk of gas eruption, oil leakage, and most importantly, they enable safe and effective extraction of hydrocarbons.

Table 2. Example of the chemical composition of a fluid used for hydraulic fracturing in gas exploration and extraction

Type of substance	Percentage by weight
Water	90.60
Solid phase (usually sand)	8.960
Acids	0.110
Substances which facilitate crushing	0.110
<b>Biocides</b>	<b>0.001</b>
Substances which prevent depositing of clayey minerals	0.050
<b>Corrosion inhibitors</b>	<b>0.001</b>
Substances which increase viscosity	0.010
Substances which reduce friction	0.050
Gelling agents	0.080
Agents which prevent the precipitation of iron	0.004
Agents which prevent the precipitation of carbonates	0.040
Surfactants and pH regulators	0.090

### Final conclusions

Corrosion as a natural problem of material deterioration will be exist. Similarly as biogenic processes, corrosion can only be limited as much as possible so as not to bring great material loss or hinder extraction. The scale of this phenomenon is immense and it concerns practically each sector of the oil and gas industry. The rational solution which

can reduce the occurrence of corrosion is the application of agents which act as potential corrosion inhibitors. Over the last few decades, the chemical industry has been working on new substances which may inhibit this process, while the composition of commonly used inhibitors is modified and improved.



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## Legal and normative acts

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