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INVESTIGATION OF CORROSION STEEL IN THE CARBON DIOXIDE ENVIRONMENT

Abstract

Corrosion of steel equipment of wells, as well as main and process pipelines, in addition to reducing their exploitation and increasing their repair costs, can cause serious damage to the environment. Damage to equipment leads to salinization of soils with aggressive reservoir water, contamination of soils and natural reservoirs with oil and oil products. In oil fields, much attention is paid to the problem of extending the service life of well processing equipment. One of the most effective ways to protect field equipment and pipelines from corrosion in the oil and gas industry is the use of corrosion inhibitors. Inhibitor protection is the most common and economically justified method of anticorrosion protection of field equipment and pipelines. By changing the dosage of the inhibitor or using inhibitors with different anti-corrosion properties, it is possible to reduce the corrosion rate to an acceptable level without fundamentally changing the existing technological schemes. Oil and gas companies have high requirements for inhibitory compositions, requiring them to have universal action.

This article provides analysis of literature sources for research of corrosion steel in carbon dioxide environment provides mechanisms of carbon dioxide corrosion of steel, as well as analysis of known inhibitors and characterizes their effect on carbon dioxide corrosion of steel. The given analysis of literature sources shows that, despite the wide range of corrosion inhibitors of domestic and foreign production, presented on the market, the problem of protection of metal equipment of gas and oil fields from carbon dioxide corrosion continues to be relevant and today the most promising is the creation inhibitors of universal action, having sufficient protective effect in conditions of hydrogen sulfide and carbon dioxide corrosion.

Recently, inorganic compounds have been widely used as inhibitors. Due to the low cost, non-toxicity and ability to protect already corrosion surfaces, phosphates have been widely used. In the presence of phosphates, a protective film is formed surface of the iron. It consists of iron hydroxide compacted with iron phosphate. Addition of polyphosphates inhibits of corrosion steel, copper, zinc, lead, and brass. Meta-and orthophosphates protect only steel from corrosion.

The study of the effect of phosphate inorganic inhibitors and their composition on corrosion steel in carbon dioxide is little studied. In this regard, research is of interest, considering that Kazakhstan has extensive reserves of substandard phosphate raw materials, which can serve as a source for synthesis of phosphate composition and for obtaining domestic inhibitors with high protective properties.

Keywords: metal corrosion, inhibitors, carbon dioxide environment, gas field, pipelines, steels, corrosion.

Introduction. Ensuring reliability and durability of operation of industrial equipment and pipeline systems is one of the most important tasks in development of oil and gas deposits and in further transportation of crude hydrocarbon. Corrosion of steel equipment of wells, as well as main and process pipelines, in addition to reducing their exploitation and increasing their repair costs, can cause serious damage to the environment. Damage to equipment leads to salinization of soils with aggressive formation water, contamination of soils and natural reservoirs with oil and oil products [1].

In this regard, the problem of extension of exploitation of the process equipment of wells is currently being given great attention in the oil fields [2]. One effective method of anti-corrosion

protection of field equipment and pipelines in the oil and gas industry is the use of corrosion inhibitors. As the latter, individual compounds or compositions of a number of substances are used, which contribute to sharp reduction of corrosion losses of metal under harsh conditions associated to presence in process media, in addition to salts, of aggressive gases (H_2, CO_2, O_2). Inhibitory protection is the most common and economically justified method of anticorrosive protection of field equipment and pipelines [3]. By changing the dosage of the inhibitor or by using inhibitors with various anti-corrosion properties, it is possible to achieve reduction of corrosion rate to an acceptable level without fundamentally change of existing technological schemes [4].

Oil and gas companies have high requirements for inhibitory compositions, requiring universal action.

In literary sources, wells damaged by corrosion are divided into two groups: *"acidic"* wells, which contain hydrogen sulfide in products, and *"neutral"*, where corrosion is mainly due to air oxygen. Carbon dioxide, as a corrosive component of the environment, does not play a significant role in comparison with O_2 and H_2S, because at equal concentrations of CO_2 and H_2S in the well production; the effect of CO_2 on corrosion is less significant than H_2S.

The situation changed dramatically with the beginning of development of deep-lying gas condensate deposits with a formation temperature of 80-140 ° C, pressure up to 35 MP and CO_2 content in the gas up to 5% with small concentrations of H_2S. Pressure sealed oil and gas collection systems were used in the development of the deposits, which prevented the ingress of significant quantities into them air oxygen.

Carbon dioxide has thus become the main corrosive component of well production. Due to high partial pressures of CO_2, the water condensate extracted from the wells was a concentrated carbonic acid solution with a pH of 4.0–5.5. Accumulation of water condensate in the coupling gaps of the tubing string (decipher completely) resulted in catastrophic rapid destruction of them. The depth of local corrosion penetration reached 8 mm/year. For the first time, carbon dioxide corrosion resulted in a problem, without which it is impossible to ensure normal operation of wells and pipelines.

Carbon dioxide corrosion is typical for most deposits in Kazakhstan. The concentration CO_2concentration in oil and associated gas is on average 0.7–1.6 % (in some cases 4-6 %).

In the oil and gas industry, two types of systems can be identified, where corrosion due to the presence of carbon dioxide: with high and low partial CO_2 pressures.

In these cases, corrosion is due to the presence of the mineralized aqueous phase and the carbon dioxide dissolved therein.

Corrosion of steel in anoxic aqueous medium containing dissolved carbon dioxide is an electrochemical process. The mechanism of carbon dioxide corrosion of steel differs significantly from processes in solutions of strong acids: it is known that at the same value of pH, corrosion in carbon dioxide medium proceeds more intensively than in solutions of strong acids [5].

There are two hypotheses to explain the effect of carbon dioxide on the corrosion process. First, in carbonic acid solutions, along with H^+ and HCO_3 – ions, non-dissociated H_2CO_3 molecules are present, acting as a buffer to replenish H ions used for depolarization.

In strong acid solutions, hydrogen ions are delivered to the corrosive surface by diffusion; and in carbon dioxide environment, depolarization is carried out by H+ ions formed in the near-electrode layer during H_2CO_3 dissociation. Assuming that the dissociation rate of H_2CO_3 is much higher than the diffusion rate of H+ from the solution volume, it is concluded that the cathode process of carbon dioxide corrosion is not limited by diffusion restrictions. The second explanation is that H_2CO_3 is directly involved in the cathode process.

According to the first point of view [6], carbonic acid does not possess any specific aggressive action, but stimulates corrosion only through pH reduction with increased PCO_2 and compensation of H+ ions used for depolarization. This does not allow explaining experimentally observed facts of increase of carbon dioxide corrosion rate with increase of PCO_2.

The most common view [7], is that direct H_2CO_3 reduction makes major contribution to the depolarization (cathode stage) of the corrosion process in carbon dioxide corrosion. The approach developed in the works of de Waard and Milliams is considered classic to be. They proposed the following equation for depolarization of the cathode process during in carbon dioxide of corrosion steel (delayed stage):

$$H_2CO_3 + e \longrightarrow H_{АДС} + HCO_3$$

with further hydrogen removal by the recombination or electrochemical desorption (fast steps).

Assuming that the reaction is not complicated by transport constraints and proceedsin the kinetic region, de Waard and Milliams proposed the following formula for calculating of carbon dioxide corrosion rate, known as the de Waard-Milliam equation:

$$lgV_C = 6.467 - \frac{1710}{273 + t} + 0.67 lg P_{CO2}$$

where V_C- is the average surface rate of metal mass loss in $g/(m_2 \cdot h)$ in terms of corrosion depth, mm/year, and PCO_2, should be expressed in MP.

The above is true if the carbon dioxide environment does not release mineral salt precipitates. However, in many actual carbon dioxide oilfield systems, the corrosion process is complicated by the deposition of salts onto the corrosion surface. The aqueous phase of well production releases salts due to the following factors or their combination: decrease of the total pressure in the system change of temperature (for example, the probability of precipitation of calcium and iron carbonates increases with temperature); change of water chemical composition, which can be observed both in mixing water of different composition, and as a result of corrosion, when water is enriched with iron ions.

Inliterary sources [8] it is shown that in electrolytes containing carbon dioxide, the atmospheric and hydrogen sulfide corrosion inhibitors of steel such as Д-4-3, N, N-diethylamino-2-methylbutanone-3 or N, N-diethylaminoethanol are ineffective. The increase in pH in the presence of amines does not slow corrosion, on the contrary, corrosion is stimulated over a wide range of concentrations, since amines adsorbed on the metal surface prevent the formation of a protective carbonate film, but are unable to slow corrosion themselves. Corrosion becomes local in the presence of Д-4-3. The more hydrophobic amines octylamine and its higher homologues can significantly reduce of corrosion steel in carbon dioxide solutions at sufficiently high concentrations (16 g/L and 8 g/L, respectively). Based on them, compositions of IFHAN-72 and IFHAN-74 with high passivating capacity are developed. IFHAN-72 (2 g/l) exhibits a blocking effect and is capable of increasing the effective activation energy of metal dissolution. Furthermore, its penetrating ability is sufficient to protect steel coated with corrosion products. IFHAN-74 is effective at lower concentrations (0.25 g/l) than IFHAN-72, but is capable of emulsifying hydrocarbons in water and less volatile, which prevents it from being used to protect steel from carbon dioxide corrosion in the gas phase.

Lower amines and amino alcohols are widely used to protect steel from carbon dioxide corrosion. Their effect is determined not only by pH control of the medium, but also by adsorption on steel.

The authors [8] investigated the protective effect of aliphatic carboxylic acids on carbon dioxide of corrosion steel in liquid and gas phases. Unlike amine substitution of carboxylic acids as inhibitors does not accelerate of corrosion steel in the liquid phase at low inhibitor concentrations. Efficiency of carboxylate inhibitors increases with increase of their hydrophobicity and allows slowing down both anode and cathode reactions to steel, calculation of high adsorption capacity. However, the dependence of the protective effect on the acid concentration passes through the maximum due to the lowering of the pH of the solution in the presence of the inhibitor. Among the carboxylic acids studied, lauric is the most effective inhibitor of carbon dioxide corrosion. Caprylic acid at a concentration of 3.7 mmol/l inhibits the dissolution of steel in the temperature range 30-100 ° C and increases the effective activation energy of corrosion process.

The ability of a number of "AMDOR" series inhibitors [9], effective in combined environment that retarded corrosion in the presence of carbon dioxide has been studied. In the absence of hydrogen sulfide, the effectiveness of these compositions is low (the greatest protective effect (79%) in the composition of AMDOR-IK-4G at a concentration of 200 mg/l). However, this additive in a carbon

dioxide deoxidized environment stimulates the process of steel flooding. The authors [10] investigated the protective effect of amine salts of nitric acid in carbon dioxide of corrosion steel. It has been found that s the hydrocarbon radical increases from C8 to C16-18, the protective effect increases dramatically. For example, nitronates based on octene-1 stimulate carbon dioxide corrosion, and products based on dodecene-1, tetradecene-1, and a-olefin mixtures C16-C18 inhibit it with Z> 98%. It has also been found that with a branched radical structure, he protective effect is dramatically reduced because such molecules cannot form a dense layer on the surface of the metal. Therefore, preferable to use compositions or chemical compounds which will have a number of advantages over the above inhibitors and are economically and ecologically advantageous.

Recently, inorganic compounds have been widely used as inhibitors. Due to the low cost, non-toxicity and ability to protect already corrosion surfaces, phosphates have been widely used [10]. In the presence of phosphates, a protective film is formed surface of the iron. It consists of iron hydroxide compacted with iron phosphate. Addition of polyphosphates inhibits of corrosion steel, copper, zinc, lead, and brass. Meta-and orthophosphates protect only steel from corrosion.

The study of the effect of phosphate inorganic inhibitors and their composition on corrosion steel in carbon dioxide is little studied. In this regard, research is of interest, considering that Kazakhstan has extensive reserves of substandard phosphate raw materials, which can serve as a source for synthesis of phosphate composition and for obtaining domestic inhibitors with high protective properties.

Conclusion. Thus, the given analysis of literary sources shows that, despite the wide range of corrosion inhibitors of domestic and foreign production, presented on the market, the problem of protection of metal equipment of gas and oil fields continues to be relevant.

At the present, the most promising is the creation of universal-action inhibitors, having sufficient protective effect in conditions of hydrogen sulfide and carbon dioxide corrosion. The main task of the coming years is to create in Kazakhstan its own effective reagents and expand industrial production. The production of own corrosion inhibitors will reduce dependence on the import of expensive imported supplies, which necessarily need additional analytical quality control in the places of consumption.

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ТҮЙІН

Ұңғымалардың болат жабдықтарының, сондай-ақ магистральдық және технологиялық құбырлардың коррозиясы, олардың қызмет ету мерзімін қысқартумен және оларды жөндеуге кететін шығындарды арттырумен қатар, қоршаған ортаға айтарлықтай зиян келтіруі мүмкін. Жабдықтың зақымдануы топырақтың агрессивті резервуарлық сумен тұздануына, топырақ пен табиғи су қоймаларының мұнай мен мұнай өнімдерімен ластануына әкеледі. Бұл мақалада көмірқышқыл ортасында болаттың коррозиясын зерттеуге арналған әдеби көздердің талдауы, болаттың көмірқышқыл газының коррозиясының механизмдері, сондай-ақ белгілі инги-биторларға талдау жасалып, олардың болаттың көміртегі диоксиді коррозиясына әсері сипатталған. Әдеби дереккөздерге келтірілген талдау көрсеткендей, нарықта отандық және шетелдік өндірістің коррозия ингибиторларының кең ассортиментіне қарамастан, газ және мұнай кен орындарының металл жабдықтарын көмірқышқыл газынан коррозиядан қорғау мәселесі бүгінгі күні өзекті және ең перспективалы болып қала береді.

РЕЗЮМЕ

Коррозия стального оборудования скважин, а также магистральных и технологических трубопроводов, помимо уменьшения срока их эксплуатации и увеличения затрат на их ремонт, может нанести серьезный ущерб окружающей среде. Повреждение оборудования приводит к засолению почв агрессивной пластовой водой, загрязнению почв и природных водоемов нефтью и нефтепродуктами. В данной статье приведен анализ литературных источников по исследованиям коррозии стали в углекислой среде, приведены механизмы углекислотной коррозии стали, а также проведен анализ известных ингибиторов и охарактеризовано их влияние к углекислотной коррозии стали. Приведенный анализ литературных источников показывает, что, несмотря на широчайший ассортимент ингибиторов коррозии отечественного и зарубежного производства, представленных на рынке, проблема защиты металлического оборудования газо- и нефтепромыслов от углекислотной коррозии продолжает оставаться актуальной и на сегодняшний день наиболее перспективным является создание ингибиторов универсального действия, обладающих достаточным защитным эффектом в условиях сероводородной и углекислотной коррозии.