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CORROSION AND SALINE DEPOSITION PROTECTION OF GAS AND OIL FIELD EQUIPMENT WITH THE USE OF COMBINED CORROSION AND SALINE DEPOSITION INHIBITORS AND MULTIFUNCTIONAL INHIBITORS

Gas and oil field equipment corrosion, caused by carbon dioxide CO_2, and saline deposits on the surface of downhole equipment are essential complications at exploitation of oil and gas wells of many fields in Ukraine, particularly the fields of OGPE "Poltavanaftogaz". Enough often these complications occur simultaneously. In the conditions of Ukraine the most effective method of ńorrosion and saline deposition protection of gas and oil field equipment is a chemical one, that is the use of inhibitors. Combined use of corrosion and saline deposition inhibitors as well as multifunctional inhibitors is one of the possible and perspective variants of inhibitor protection in conditions of corrosion under the action of carbon dioxide and saline deposition. Therefore when choosing inhibitors it is very important to take into account the reasons causing inaccuracies and errors at determining of their protective properties.

In practice when using inhibitors the insufficient account of local conditions and discrepancy between protection efficiency on standard samples and actual value of efficiency take place. This deals for instance with differences in properties of laboratory metal sample surface or corrosion sensor and those of the surface of real protected equipment. For instance, a considerable error takes a place when determining parameters which characterize efficiency of action of corrosion inhibitors (degree of anti-corrosive protective action and efficiency coefficient). Thus, in the case of corrosion under the action of carbon dioxide CO_2, which takes place in many gas and gas-condensate fields of OGPE "Poltavanaftogaz", formation of mineral sediments is possible on the surface of equipment. These sediments contain the products of corrosion, hydrocarbon phase and mechanical admixtures. They can

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substantially influence accuracy of determining carbon steel corrosion rate and as a result – the accuracy of determining the degree of anti-corrosive protective action and efficiency coefficient. The change of properties of corrosive environment in time also has influence on protection efficiency. For instance, efficiency of hydrocarbon-dissolving inhibitors decreases when water content in the production of well increases.

The difference between condition of the protected intra-well equipment surface and the one of laboratory metallic samples is also the reason of discrepancy of the results when using gravimetric method for determining corrosion inhibitor efficiency. As experience shows the laboratory metallic samples which are placed in the stream of liquid or gas, produced from wells, have a clean surface, and downhole equipment has been covered with the products of corrosion and sediments. Some corrosion inhibitors are better adsorbed on the clean surface, others – on the surface, covered with sediments. For example, efficiency of reagents "Нефтехим-1", ГИПХ-4, КРЦ-3, КРЦ-А and some other is higher on the samples, covered by the products of corrosion or the layer of sediments, than on the clean metal. Obviously, that these inhibitors or analogical ones on adsorption ability at field tests and estimation of their efficiency by gravimetric method (measuring of loss of mass of samples) couldn't shaw positive results and will not be used. Nevertheless in the conditions when an equipment is exploited for a long time and covered with the layer of sediments, these inhibitors can provide maximum protection [1].

By gas and oil industry for protection of gas and oil field equipment against corrosion, caused by carbon dioxide, the following inhibitors are used: И-1-А, АНПО, ККС-12, Газохим-1, СЕКАНГАЗ, ИФХАНГАЗ-1 [2], "Нефтехим-1", ГИПХ-3, ГИПХ-4, ГРМ, КРЦ-3, КРЦ-А, АНП-2, ВЖС, ИКСГ-1, КО, К-1-УК, СТ-1, КМА, "И1", "И2-И11", water and oil soluble inhibitor "1 НКО", the complex corrosion and gas hydrate formation inhibitor "КИНГ" [3], complex inhibitors and corrosion inhibitors of multifunction action ИКИПГ, ДИК – 1, И – 25 – ДМ, И – 25 – Д, КАЗ – И, "Амфикор", "Коразол", lubricating materials on the basis of the modified rape oil, nitrogen-containing lubricating materials on the basis of phenolic and quinoid derivatives of benzotriazol [4], ТАЛ-3, "Тарин", multifunctional corrosion inhibitors БКМ, БКФ, ВТІБФОЛ [5], imported inhibitors Додіфлоу 3421, Додікор V3314, IRGAKOR L-184, et al.

Deposition of mineral salts in wells and oil field structures is a serious problem when producing oil and gas. The problem is complicated when hard-soluble salts are deposited. These are such salts as sulphates of calcium, barium and strontium; and carbonates of calcium, magnesium, barium and strontium.

As a rule saline deposits are displayed on the late stage of development of fields at the active inflow of stratal waters. The main reasons of deposition of mineral salts on the gas and oil field equipment surface are following [6]: decomposition of dissolved in water bicarbonate salts of calcium and magnesium because of change of thermodynamic conditions (pressure decrease), mixing in a stratum and well waters of different compositions (for example, injected and stratal waters, edge and bottom waters), mixing in the producing wells waters from different strata and interlayers and contact of water (stratal and injected) filtering in a stratum with a rock.

The presence in composition of salts sulphates of calcium and carbonates of calcium, magnesium and magnesium complicates prevention of saline deposits on the gas and oil field equipment surface.

Saline deposition in well and more exactly in the bottom-hole formation zone and on the gas and oil field equipment surface result in such serious consequences as premature breakdown of submersible electric centrifugal pumps and gas lift valves, plugging and tear of field communications, sharp decline of the productivity of producing wells and injectivity of injection wells et al. The main methods of prevention and removal of saline deposition on the gas and oil field equipment surface are the following : limitation of production rate, pumping of inhibitor to the wellhead, pumping of inhibitor through the column of pipes of small diameter to the well bottom and pumping of inhibitor to the stratum under pressure in the way that it is slowly consumed when producing gas. The variant of pumping of inhibitor directly to the bottom-hole formation zone is discussed in detail in [7].

The inhibitors of saline deposition embrace the wide spectrum of reagents. The main among them are anionic phosphororganic inhibitors (phosphonic acids), anionic inorganic poliphosphates and inhibitors on the basis of polymeric compound of acryl row. The first group of the inhibitors of saline deposition has been presented by nitrilootrimethylphosphonic acid (НТФ), compositions, got on the basis of НТФ – ИСБ-279, ИСБ-281, НТФ-ЕГ, oxyethylidenediphosphonic acid (ОЭДФ), polyaminomethylphosphonic acids (ПАФ) and diaminopropanol of tetramethylphosphonic acids (ДПФ). On the basis of НТФ, ОЭДФ, ПАФ and ДПФ with addition of water, ethylene glycol and other components the inhibitors of saline deposits such as ПАФ – 1, ПАФ – 13, ДПФ – 1, СНПХ – 5301, phosphonol, číęđĺäîë-1 have been got [8]. The second group includes the sodium polyphosphate (ПФН), trisodium polyphosphate (ТПФН), sodium hexametaphosphate (ГМФН), trisodium phosphate (ТНФ). The third group has been presented by hydrolysed polyacrylamid (ПАА) and hydrolysed polyacrylonitrile. The group of multicomponent inhibitors of saline deposits include the reagent ПС-АзНДПИнефть (it is the composition on the basis of ammonium, ammophosphate and sulphanol), the mixture of liquid ИСТ-1 on the basis of phosphororganic compound and sulphanol, the reagent “Азербайджан” (the mixture of water solution of sodium silicate and ethyl spirit) and imported inhibitors (SP-181, SP-191K, корексит-7647 et al). There are also inhibitors of saline deposits on the basis of nitrogen containing compounds, triethanolamine salts of primary fat alcohols et al.

As many researchers mark, the task of efficiency increase of corrosion and saline deposition protection of gas and oil field equipment is to be solved by the increase of inhibiting ability of reagents at simultaneous enlargement and reduction of prices of their assortment. This could be achieved by using of industrial wastes and plant raw. This task could be solved in two ways: by combined using of corrosion and saline deposition inhibitors and with the help of multifunctional inhibitors. For combined corrosion and saline deposition protection of gas and oil field equipment the following compositions of reagents and multifunction inhibitors are used: compositions, containing 0.7...0.8% of neonol and microdoses of inhibitors of saline deposits of bifunctional action, possessing complex properties [9] (that is they have high surface activity and could be used for inhibiting corrosion and saline

deposition); the mixture of inhibitor of saline deposition ИСБ-1 and corrosion inhibitor Дигазфен-1 [10]; inhibiting compositions on the basis of nitrogen containing foams for corrosion and saline deposition protection of gas and oil field equipment and simultaneously for water carrying away from gas and condensate well bottoms [11]; multifunction reagents (antiscaling reagents and corrosion inhibitors) ОЭДФК АФОН 200-60А, АФОН 230-23А, ИОМС-1 [12] et al.

In the Ivano-Frankivsk national technical university of oil and gas laboratory researches have been carried out on determining of efficiency of multifunctional action reagent "Коразол" and of the mixture of saline deposition inhibitor КТІ-С and corrosion inhibitor ŇŔË-3. The degree of corrosion protection and the degree of diminishing of saline deposition intensity were determined in mineralized water with mineralization of 100 g/l at the temperature of 90 ^{o}C on laboratory samples of steel Р-110. Laboratory researches have been carried out with the concentrations of reagents 0.05, 0.1, 0.25, 0.5 and 1% of mass. in mineralized water. By the results of laboratory researches the optimum concentration of reagents in mineralized water have been determined. It was equal to 0.25% of mass. For 0.25% of mass. solution of reagent "Коразол" in mineralized water the degree of corrosion protection is equal to 97.5% and the degree of diminishing of saline deposition intensity is equal to 83.85% , and for 0.25% of mass. solution of mixture of reagents КТІ-С and ТАЛ-3 in mineralized water the degree of corrosion protection is equal to 83.7% and the degree of diminishing of saline deposition intensity is equal to 78.4%. Both reagents "Коразол" and the mixture of КТІ-С and ТАЛ-3 are water and hydrocarbon soluble, that is they are universal reagents and do not form hard destroyable emulsions. Besides these inhibitors are cheap, untoxic and ecologically safe because they are got of the industrial wastes and plant raw. The technology of corrosion and saline deposition protection of gas and oil field equipment by combined using of corrosion and saline deposition inhibitors and with the help of multifunctional inhibitors consists of preparation of the solution of reagent "Коразол" or mixtures of reagents of КТІ-С and ТАЛ-3 in mineralized water of necessary concentration near the well and pumping of the prepared solution into the well. It is recommended to carry out pumping of the reagent / the mixture of reagents to annular space of well by a pumping unit or an inhibitor tank.

CONCLUSIONS

1. The insufficient account of local conditions is the substantial disadvantage of inhibitor corrosion protection in oil and gas fields. This results in discrepancy between protection efficiency when determining on standard samples and actual value of efficiency. One of the main reason of it is difference in properties of laboratory metallic sample surface or sensor of corrosion and the surface of real protected equipment. Therefore when doing estimation of corrosion inhibitor efficiency and saline deposition inhibitor efficiency it is very important to take into account the reasons causing inaccuracies and errors of determining of their protective properties.

2. Gas and oil field equipment corrosion, caused by carbon dioxide, and saline deposition on the equipment surface often simultaneously. Therefore for protection of equipment it is expedient to use corrosion and saline deposition inhibitors jointly and multifunctional inhibitors.
3. The task of efficiency increase of corrosion and saline deposition protection of gas and oil field equipment has to be solved by the increase of inhibiting ability of inhibitors at simultaneous enlargement and reduction of prices of their assortment. It is possible to achieve this by using of industrial wastes and plant raw.
4. By the results of laboratory researches carried out in the Ivano-Frankivsk national technical university of oil and gas the conclusion has been drawn about high efficiency of reagent of multifunctional action "Коразол" and of the mixture of reagents KTI-C and ТАЛ-3. This is proved by the values of the degree of corrosion protection and the degree of diminishing of saline deposition intensity for reagent "Коразол" and the mixture of reagents KTI-C and ТАЛ-3.

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