PROTECTING STEELS AGAINST CORROSION AND THE FORMATIONOF MINERAL SALT DEPOSITS

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Abstract: The paper studies the physicochemical properties of import-substituted and export-oriented nitrogen, amine and phosphorus new composite inhibitors for corrosion protection of steels as well as scaling obtained from local raw materials and industrial wastes. Inhibiting properties of corrosion and mineral salt deposit accumulation in acid and hydrogen sulfide environments have been determined. It was found that the efficiency of the inhibition process with the use of composite inhibitors in acidic and hydrogen sulfide environments obeys the Langmuir law. The values of activation energy of the adsorption process in these media and thermodynamic values *(ΔH, ΔS, ΔG).*

Keywords: inhibition, thermodynamics, corrosion of steels, inhibitor, protective mechanism, activation energy, Gibbs energy, corrosion rate, hydrogen sulfide.

Introduction. Globally, corrosion protection of steel is one of the most important scientific, technical and economic problems. Because in industrially developed countries losses from corrosion of metals makeup from 2 to 4% of gross national product [1-3]. In the Republic of Uzbekistan, industrial scale as a result of research works has achieved significant results in studying the effect of inhibitors on corrosion of metal equipment, creation and implementation of new import-substituting, export-oriented, competitive inhibitors meeting the requirements of international standards, providing high efficiency even at low concentrations, safe in the application of new universal corrosion inhibitors. In this relation, the most effective neutral and weakly alkaline media inhibitors are nitrogen, amine, and oxygen-containing organic compounds [4-6], as well as organophosphorus zinc acids which effectively prevent corrosion and mineral salt deposits on equipment surfaces.

Materials and methods of research. The object of the study is multi-component composite inhibitors created on the basis of nitrogen, amine and phosphorus-containing substances and the subject of the study includes the study of general patterns of inhibitor application mechanisms for anticorrosion protection and against the mineral salt build-up of steel samples using modern methods of physical and chemical analysis. Materials for research were the samples in the form of metal plates made of steel St.3 and St.12. Influence of nitrogen and phosphate-containing inhibitors on steel St.3 and St.12 corrosion rate was investigated by the gravimetric method in the model environment and using $5 \cdot 10^{-3}$ mol/l solution of H_2SO_4 (background). In addition, experiments were conducted in 1-3% aqueous solution of NaCI, NaOH and 1-3% aqueous solution of Na_2S in the presence of H_2S. The duration of the tests was 48 and 760 hours. The inhibitors are a transparent liquid mass, well soluble in aqueous and acidic media. No independent phase formation was observed during storage.

Results and their discussion. Experimental data on the dependence of the inhibition process on concentration and temperature on the degree of corrosion protection of steel samples of St.3 and 12 grades in the presence of inhibitors and without them showed that the applied composite inhibitors synthesized on the basis of nitrogen, amine and phosphorus-containing local raw materials and processing waste have the protection degree at 25°C 88.5-94.4%, and at 40÷50°C this index is in the range 89.0÷99.7%. If the process temperature goes up to 70°C, the degree of anti-corrosion protection beginsto decrease slightly up to values of 99.3÷90.4%.

Using the gravimetric method based on time, temperature, inhibitor concentration and other indices it has been determined that during the process in aqueous, acidic and neutral medium, at increasing inhibitor concentration from 0.1% to 1.0% the index of corrosion protection is equal to 96.2%÷99.8%. The corrosion protection rate of imported inhibitors of the Nalco brand in our Republic is 87.6% at the temperature of 80°C. It is known that inhibition of acid corrosion of metals by organic compounds is caused mainly by surface shielding and activation factor (an increase of activation energy of corrosion process in the presence of inhibitors in relation to background). To

calculate activation energy, we plotted **lgK-1/T** (Fig. 1). Studies on corrosion of St.3 and St.12 in acidic solutions in the presence of inhibitors containing amino- and phosphate groups showed their high efficiency.
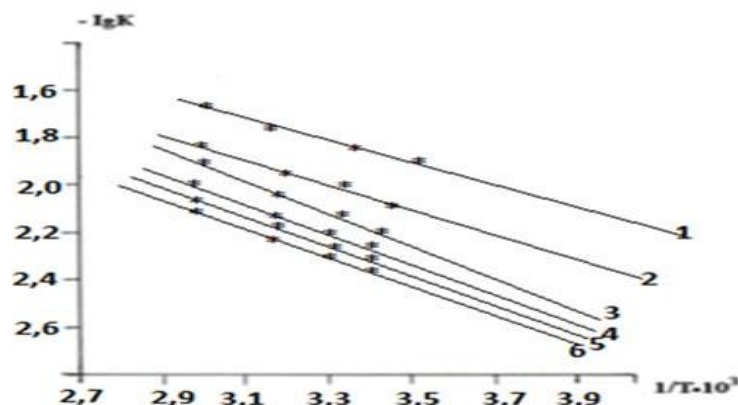

Fig.1. Dependence of lgK on the inverse temperature of the corrosion process ofsteels St.3 and St.12:

1 - Background; 2 - Sinh -1.0 mol/l; 3 - Sinh -1.25 mol/l; 4 - Sinh -2.5 mol/l; 5 - Sing -5.0 mol/l; 6 - Sinh -10.0 mol/l.

The best inhibitor of corrosion of St.3 in the studied conditions recognized, in a series of alkylamines, phosphate-diethylmethacrylate, apparently because of the large number of radicals in its molecule and their size, so that the required protective concentration of this inhibiting system is minimal, in comparison with the other studied amines. From the IgK-1/T dependence plot with the value of the slope tangent, the effective activation energy was calculated (E_{act} =2,3Rtgα). The value of E_{act} was found to be 28.5÷47 kJ/mol. The **Eact, ΔH and ΔS** of multicomponent composite inhibitors containing nitrogen, amine and phosphorus in a strong acid medium have beendetermined. The results are given in table 1.

Table 1

Thermodynamic values for corrosion in 3% Na2 S solution media involving 3% H2 SO4 and H2 S (T=298K; Sing =1.0%)

Alloy sample	Background inhibition	Eact, kJ/mol	ΔH, Dj/mol	ΔS, Dj/mol
St. 3	3% H2 SO4	39,88	37,48	70,49
St. 12		76,54	-41,82	48,64
St. 3	H2S with involvement 3% Na2S	37,48	38,25	69,75
St. 12		59,56	-70,04	39,51

The results give a good explanation for the Langmuir isotherm about the high degree of filling of the metal surface directly proportional to the dependence of the adsorption process with the concentration of nitrogen, amine and phosphorus- containing composite inhibitors. In addition, the dissolution rate (K) of metal samples depends on the content of inhibitors and even if the inhibitor is of low concentration the degree of corrosion resistance will be 96-99.6%. At the introduction of composite inhibitor in the medium of 3% H2 SO4 solution in the temperature range 298÷343K the values of Gibbs energy ΔG_{ads} change from -48.24 kJ/mol^{-1} to -42.52 kJ/mol^{-1}. The correlation of process temperature along the direction of Langmuir adsorption isotherm in alkaline-saline aggressive media for steel samples of St.3 and St.12 grades at temperature intervals 298÷343K with nitrogen, amine and phosphorus-containing inhibitors had different degrees of anticorrosive protection of metal samples. At the same time, increasing the processing time from

240 to 360 hours increases the degree of corrosion protection to 92.9÷96.7%. This indicates that multiple phases exist on the metal surface and that they do not dissolve simultaneously. Under conditions of H_2S solution background, indices of corrosion rate of steel sample St.3 during 3-4 hours are approximately the same and it proves that corrosion process in aggressive media occurs at high speed. When inhibitor concentration increases from 0,001 to 1% the protection efficiency of the inhibitor used increases from 92.3% to 99.2% respectively. This change is also observed at temperatures of 313, 323 and 343K.

Composite corrosion inhibitors involving zinc oxide, glycerine, caustic soda, sodium hydroxide and the cube residue of methyl ethyl ammonium reagents based on oxyethylene phosphonic acid, A composite inhibitor was tested on equipment and pipelines of Shurtan gas chemical complex for corrosion resistance, including prevention of mineral salts formation by comparing performance of **Option and Nalco** inhibitors supplied from abroad**.** The results of the tests at SHCC are shown in Table 2.

Table 2

Corrosion protection performance of nitrogen, amine and phosphorus inhibitors

Inhibitor compositions	Corrosion inhibition efficiency, %	Efficiency from formation of mineralsalts, %
1	97,8	94,8
2	96,8	95,2
3	98,4	97,7
4	93,3	92,5
5	91,5	88,6
Option brand comparison inhibitor	96,6	90,1

Conclusion. The results of the research showed the prospects of using nitrogen, amine and phosphorus-containing inhibitors derived from local raw materials and industrial wastes of the Republic of Uzbekistan. The optimum concentrations of inhibitors for the protection of metals against corrosion and prevention of the formation of mineral deposits in acid and hydrogen sulfide environments have been established. It is shown that the coating speed of composite inhibitors on the steel sample surface (St. 3 and St. 12) passes in one plane and is realized by the Langmuir law with the formation of layer preventing metal corrosion and activation energy in these media of steel St. 3 and St. 12 with inhibitors application is determined. On the basis of the calculated thermodynamic functions (ΔH, ΔS, ΔG) it is found that the Gibbs energy has a negative value (ΔG_{eff}). In order to import substitution of inhibitors the mechanisms and indicators of inhibition of metal corrosion process as well as prevention of formation of mineral salt deposits in acid, hydrogen sulfide, alkaline-saline and water aggressive media have been studied and optimal concentrations of multicomponent inhibitors for different media have been established.

The composite inhibitors are used to increase the inhibition efficiency of mineral salt accumulation by 2-6% and increase the corrosion protection of metals to 98.4%.

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SUYULTIRILGAN GAZLARNI SAQLASH MASALALARINI O'RGANISH

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Hozirgi vaqtda suyultirilgan tabiiy gaz global uglevodorod bozorida tobora muhim rol o'ynamoqda. Suyultirilgan tabiiy gaz iste'molining ko'payishi nafaqat ayrim mamlakatlar va mintaqalarda o'z energiya resurslarining yetishmasligi, balki, avvalambor, suyultirilgan tabiiy gazning boshqa energiya manbalariga nisbatan sezilarli afzalliklari bilan bog'liq. Birinchidan, suyultirilgan tabiiy gazni etkazib berish uchun gaz quvurlari tizimini, shu jumladan borish qiyin bo'lgan joylarda qurish va texnik xizmat ko'rsatishning hojati yo'q. Suyultirilgan tabiiy gazning asosiy afzalligi uni dengiz orqali uzoq masofalarga tashish, okeanlararo etkazib berishni amalga oshirish va eng past narxlarda bozorlarda sotish qobiliyatidir. Bu ayniqsa, energiya xavfsizligini mustahkamlash va gaz eksportini diversifikatsiya qilishga intilayotgan O'zbekiston uchun to'g'ri keladi. Ikkinchidan, suyultirilgan tabiiy gaz quvur liniyasiga nisbatan yuqori sifat bilan tavsiflanadi. Buning sababi shundaki, suyultirish jarayonida gaz zararli aralashmalar va oltingugurt birikmalaridan tozalanadi, shuning uchun chiqishda metan miqdori yuqori bo'lgan deyarli toza gaz olinadi. Bundan tashqari, suyultirilgan tabiiy gaz uglevodorod elektr energiyasi olishda ekologik toza manba hisoblanadi.

Bugungi kunda suyultirilgan tabiiy gazning global bozori juda tez sur'atlar bilan rivojlanmoqda. Yangi eksportchilar va importchilar paydo bo'lmoqda, gazni suyultirish texnologiyalari takomillashtirilmoqda, suyultirilgan tabiiy gazni tashish va saqlash sohasidagi eng zamonaviy innovatsion echimlar va ishlanmalar qo'llanilmoqda, ishlab chiqarish va qayta gazlashtirish quvvati oshirilmoqda.

Suyultirilgan tabiiy gazni suyultirish, berish va qabul qilish uchun yuqori texnologiyali komplekslarning ajralmas qismi bu katta hajmli er usti izotermik tanklardir. Suyultirilgan tabiiy gazning katta hajmli rezervuarlari katta hajmdagi yong'in va portlash xavfi bo'lgan mahsulotning omborlari bo'lib, ularning bosimi mahsulotning atmosferaga chiqishi bilan favfli oqibatlarga olib kelishi mumkin. Shu bilan birga, bunday tanklarni loyihalash, qurish va ulardan foydalanishning me'yoriy-huquqiy bazasi va amaliyoti deyarli yo'q. Bunday vaziyatda, qiyin sharoitlarga moslashtirilmagan izotermik saqlash bo'yicha horijiy loyihalar amalga oshirilmoqda, bu suyultirilgan tabiiy gaz rezervuarlarining xavfsiz ishlashi bilan bog'liq muammolarga olib kelishi mumkin.

Izotermik tanklarda suyultirilgan tabiiy gaz mavjud bo'lganda, tashqi issiqlik oqimlariga bog'liq bo'lgan tanklarning issiqlik rejimi katta ahamiyatga ega. Shu nuqtai nazardan, kriogen suyuqlikning zichligi bo'yicha tabaqalanish sodir bo'lganda, bunday vaziyatni hisobga olish kerak, bu suyuqlik qatlamlarini bug' hosil bo'lishi bilan keskin o'z-o'zidan aralashishiga va suyultirilgan