UDC 665.61.543.32

DEVELOPMENT AND STUDY OF INHIBITOR TO PREVENT INORGANIC SALTS DEPOSITION

Kh.I. Hasanov, N.N. Khalilov

«Oil Gas Scientific Research Project» Institute, SOCAR, Baku, Azerbaijan
H. Zardabi 88a, AZ 1012, Baku
E-mail: x.qasanov58@gmail.com

Received 29.04.2022
Accepted 02.06.2022

Abstract: *The paper deals with potential compositions developed for inhibiting scale deposition on oil refining equipment and pipelines based on inhibited hydrochloric acid, dispersant EC 9660A, laprol 4202-2B-30 and water. The density of the produced compositions at 20 ºC is 1020-1050 kg/m^3, the kinematic viscosity at 20 ºC is 30-40 mm^2/s, the pour point is minus 5-15 ºC, the hydrogen index pH = 2-3. The efficiency of scale inhibition was evaluated by means of common practice which relies on the ability of the chemical to retain calcium and magnesium cations in simulated artificial mineral water. It was established that the compositions at a consumption rate of 50 mg/l generate a better protective effect (76.3-85.6 %) as compared to cases when the inhibitor consumption was 40 mg/l (73.1-83.2 %) and 30 mg/l (70.4-78.1 %). The compositions with 10 % of mass fraction of laprol 4202-2B-30 have demonstrated higher protective properties.*

Keywords: *scale inhibitor, inhibited hydrochloric acid, surfactant, inhibition efficiency, calcium sulfate, active agent.*

DOI: 10.32737/2221-8688-2022-2-175-182

Introduction

Problems arising from the oil refining services may, in some way, be caused by the formation of complex salt deposits in oil collection, transportation and treatment systems. As for the predominant content in the deposits of certain types of inorganic salts, two groups of salt are specified: carbonate and sulfate. The most common type of deposits of inorganic salts is deposits containing mainly sulfates and carbonates of calcium and magnesium. The composition of deposits in the form of impurities contains oxides of iron and silica, the presence of which is explained by corrosion of oil refining equipment and pipelines. The formation of precipitation results in the damage of valuable equipment, along with time consuming maintenance activities. In an effort to eliminate the build-up of scales the companies are annually faced with costs in the form of lost products [1].

The most effective means of controlling the scale is the use of inhibitors. Inhibitors are designed to prevent the build-up of mineral deposits of various compositions on the inner surface of oil refining equipment, pipelines, collection and transportation systems of water-cut crude, formation pressure maintenance systems and wastewater disposal.

The use of chemicals is the most effective and streamlined way to prevent deposition of inorganic salts. At the moment, the oil industry can largely benefit from the availability of sufficient number of scale inhibitors [2].

Considering the properties and mode of action on supersaturated solutions, scale inhibitors are divided into “threshold” and mixed action chemicals as well as complexing agents [3–5].

It found that inhibitors with a “threshold effect” exhibit the greatest protective effect [1, 3]. This type of inhibitors forms a protective film on the surface of salt “nucleation”, helps to retard their growth, and resist when crystals are

connected to each other and on the surface of the protected equipment.

Complexing inhibitors generate water-soluble anionic or chelate complexes with alkaline earth metal cations. Mixed action reagents demonstrate both "threshold" properties and properties of complexing agents [6, 7].

To ensure effective protection of equipment, the scale inhibitor selected for certain conditions is required to be permanently present in the required amount in the system. The maximum protective effect can be obtained if the inhibitor is injected into the solution before the beginning of crystallization of inorganic salts [1, 8–11].

Following from cost-effectiveness and considering the nature and conditions of well development, the availability of engineering tools and other factors, various techniques can be applied, however, in oilfield practice, inhibitory methods of protection have received priority to prevent complications associated with scaling and corrosion of equipment.

The purpose of this work is to produce chemicals on the basis of inhibited hydrochloric acid and surface-active substances (SAS), and to analyze them as scale inhibitors.

Practical part

The technical result of this work is to exclude the use of scarce, expensive chemicals such as SNPX 5312C, Incredol, PAF-13, FLOSPERSE HT, FLOSPERSE DISSOLVER, FLOSPERSE PX60N to prevent the deposition of inorganic salts during oil and gas processing on equipment and pipelines of carbonate and terrigenous formations containing hydrochloric acid and SAS [12].

One of the main requirements to scale inhibitors is their adsorption-desorption properties [13, 14]. In this respect the use of chemicals reducing the interfacial tension at the boundary of the oil-inhibiting solution is required to improve the adsorption-desorption characteristics of the scale inhibitor. Due to the adsorption-desorption characteristics, the produced chemicals act as scale inhibitor for a long time and show high efficiency. Treatment of the surface of productive rocks with an inhibitory composition containing hydrochloric acid reduces the surface tension at the “rock-oil-inhibiting solution” interface and makes it possible to better prepare the rock surface for adsorption due to the rejection of film oil and hydrophilization of the surface [15]. At the same time, there is also an increase in the roughness of the rock due to the chemical interaction of hydrochloric acid with carbonate minerals. Besides, hydrochloric acid can clear the surface of the rock from film oil, changing its wettability and, thereby, ensuring uniform and complete adsorption of the scale inhibitor.

Compositions were developed for inhibiting scale deposition on oil refining equipment and pipelines based on inhibited hydrochloric acid, dispersant EC 9660A, laprol 4202-2B-30 and water.

As a constituent of the inhibitor, hydrochloric acid rids the bottom-hole formation zone,

tubing of salt and paraffin-tar deposits. It acts on the rocks of the bottom-hole formation zone creating looseness and etching channels which leads to better permeability and well productivity. Addition of a nonionic SAS (laprol 4202-2B-30) to the solution reduces the value of interfacial tension. As a nonionic SAS, it is adsorbed on asphaltene-resin-paraffin deposits (ARPD) and helps to reduce the surface tension at the interface with the solvent. As a result, the efficiency of dissolution and destruction of ARPD increases. For this reason, the viscosity of oil decreases. The dispersant EC 9660A helps to reduce the surface tension at the interface and thus acts as an auxiliary agent for the action of the nonionic SAS.

The components contained in the composition of the inhibitor, specifically hydrochloric acid, is used in the form of a 21 % aqueous solution. Dispersant EC 9660A is manufactured by Nalco Europe B.V. When preparing the inhibiting compositions, the dispersant EC 9660A was used in the form of a 35 % aqueous solution. Laprol 4202-2B-30 was procured from PJSC “Nizhnekamskneftekhim”.

Table 1 indicates the results of the work to produce scale inhibitors.

Table 1. Results of preparation of scale inhibitors based on inhibited hydrochloric acid and SAS

№ of sample	Amount of substances in the composition, % mass.			
	Inhibited hydrochloric acid	Dispersant EC 9660A	Laprol 4202-2B-30	Water
1	25	18	8	49
2	30	18	8	44
3	30	20	8	42
4	30	22	8	40
5	30	18	10	42
6	30	20	10	40
7	30	22	10	38
8	30	18	12	40
9	30	22	12	36

According to the Table, inhibited hydrochloric acid is 25-30 %, dispersant EC-9660A 18-22 %, laprol 4202-2B-30 8-12 %, water 36-49 % in the compositions of the scale inhibitor.

The density of the produced compositions at 20 ^{0}C is 1020-1050 kg/m^3, the kinematic viscosity at 20 ^{0}C is 30-40 mm^2/s, the pour point is minus 5-15 ^{0}C, the hydrogen index (pH) is 2-3. The compositions are clear, red-brown liquids.

The efficiency of scaling inhibition was evaluated using a common practice based on the ability of the chemical to retain Ca^{2+} and Mg^{2+} cations in artificial mineral water simulating formation water [16]:

$CaCl_2$	13.6 g/dm^3
$MgCl_2 \cdot 6\ H_2O$	1.2 g/dm^3
Na_2SO_4	13.0 g/dm^3
NaCl	18.8 g/dm^3

As required by the testing procedure [15], when the inhibitor is poured into the prepared water, which simulates formation water, it is placed in a thermostat at a temperature of 80^{o}C and kept for 5 hours. At the same time, a control sample is placed without the addition of the chemical. After cooling the samples, the precipitates are filtered. In filtrates, the content of calcium and magnesium ions is determined by trilonometry [15].

The protective effect of inhibition of inorganic salts was determined by:

$$Э,\ \% = (C_i - C_{w/o}) / (C_0 - C_{w/o}) \times 100,$$

where C_i, $C_{w/o}$ and C_0 are respectively the concentration of a salt forming ion in a solution with an inhibitor, mg/l; without inhibitor, mg/l; and in the source water with the initial concentration, mg/l.

Results and discussion

The results of the work made it possible to determine the protective effect of the prepared inhibitors as shown in Table 2. For the purpose of comparison, the inhibition effect of the known chemicals on scaling in simulated solutions is shown in Table 3.

Table 2. Results of work to determine the protective effect of inhibitors

№ of sample	Inhibitor composition	Inhibitor consumption, mg/l	Protective effect of inhibitor, %
1	19.55 % active agent, 80.45 % water	30 40 50	70.4 73.1 76.3
2	20.6 % active agent, 79.4 % water	30 40 50	71.7 74.3 77.5
3	21.3 % active agent, 78.7 % water	30 40 50	74.4 76.3 78.4
4	22.0 % active agent, 78.0 % water	30 40 50	75.4 77.5 80.1
5	22.6 % active agent, 77.4 % water	30 40 50	75.9 78.2 80.8
6	23.3 % active agent, 76.7 % water	30 40 50	78.1 83.2 85.6
7	24.0 % active agent, 76.0 % water	30 40 50	75.1 77.2 79.3
8	24.6 % active agent, 75.4 % water	30 40 50	74.7 76.3 77.1
9	26.0 % active agent, 74.0 % water	30 40 50	71.7 74.2 76.8

As seen from Table 2, the active substance in the compositions is 19.55-26.0 %. The addition of the prepared compositions to the calcium and magnesium sulfate solution at a consumption rate of 50 mg/l leads to a high protective effect (76.3-85.6 %) as compared to cases in which the inhibitor consumption was 40 mg/l (73.1-83.2 %) and 30 mg/l (70.4-78.1 %). Compositions of samples 3-6 exhibit better protective effect. A distinctive feature of these compositions is that the mass fraction of laprol 4202-2B-30 is 10 %. The presence of a nonionic SAS in the composition of the scale inhibitor below and above 10% leads to worsening of the inhibition quality.

Table 3. The inhibition effect of the known chemicals on scaling in simulated solutions.

№ of a sample	Inhibitor brand name	Dosage, mg/l	Effectiveness, %
1	SNPX 5312C	40	73,9
2	Incredol	40	69,8
3	PAF-13	40	68,1
4	FLOSPERSE HT	40	70,3
5	FLOSPERSE DISSOLVER	40	69,8
6	FLOSPERSE PX60N	40	71,7

The results of determining the protective effect of various scale inhibitor formulations are given in Fig.1-3.

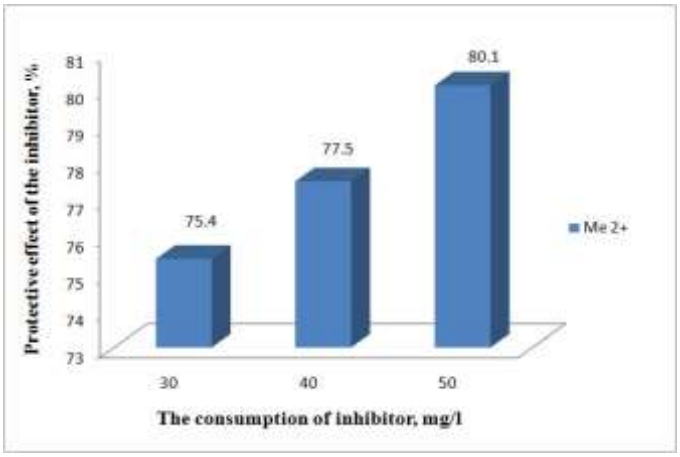

Fig.1. Correlation between the protective effect of the scale inhibitor (22 % active substance, 78 % water) and inhibitor consumption

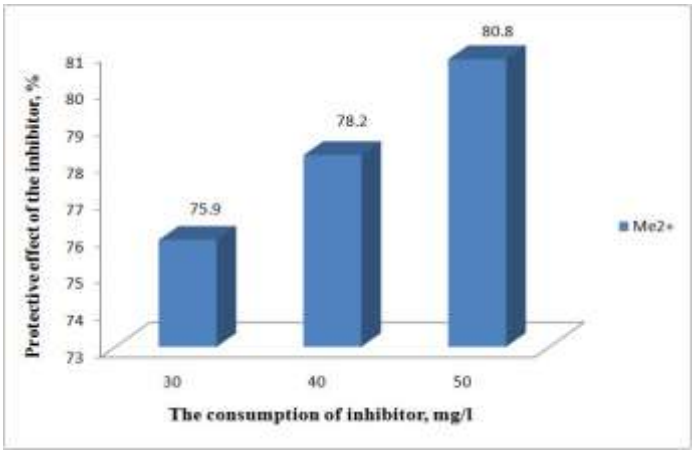

Fig. 2. Correlation between the protective effect of the scale inhibitor (22.6 % active substance, 77.4 % water) and inhibitor consumption

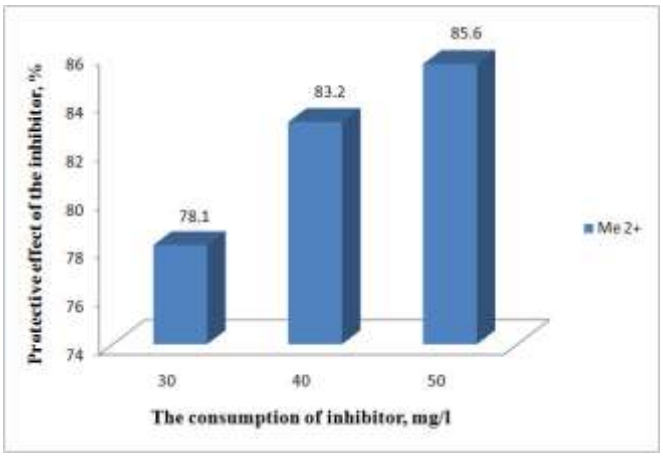

Fig. 3. Correlation between the protective effect of the scale inhibitor (23.3 % active substance, 76.7 % water) and inhibitor consumption

In the summary, proper compositions were developed to prevent the scale deposition on oil refining equipment and pipelines based on inhibited hydrochloric acid, dispersant EC 9660A, laprol 4202-2B-30 and water. The efficiency of scale inhibition was evaluated by common practice which relies on the ability of the chemical to retain calcium and magnesium cations in simulated artificial mineral water.

References

1. Crabtree M., Eslinger D., Fletcher P., Miller M., Johnson A., King G. Fighting-Scale: RemSoval and Prevention. *Oilfield Review*. 1999, vol. 11, no. 3, pp. 30–45.
2. Glushchenko V.N., Denisova A.V., Silin M.A., Ptashko O.A. Inhibitor protection of oilfield equipment from corrosion and scaling. Ufa : Kitap Publ., 2013. 592 p.
3. Kashchavtsev V.E., Mishchenko I.T. *Scale buildup during oil production.* Moscow: Orbita Publ., 2004. 432 p.
4. Shangaraeva L.A., Maksyutin A.V., Sultanova D.A. Methods to prevent scaling in the development and operation of oil deposits. *Modern problems of science and education.* 2015, no. 1-1; URL:http://www.science-education.ru/ru/article/view?id=19032
5. Chaplanov P.E., Polkovnichenko I.T., Toporkova N.A., Penzeneva T.A. Inhibitors of inorganic salt deposits. Background information Ser. *"Petrochemistry and oil shale processing"*. Moscow: ChNIITEneftekhim Publ., 1989, issue 5, 59 p.
6. Khalilov N.N. Scale inhibitors on phosphates of etylene-diamine and nanoparticles. *Azerbaijan Oil Industry.* 2021, no. 9, pp. 37-41. DOI.10.37474/0365-8554/2021-9-37-41
7. Hasanov Kh.I., Khalilov N.N. Salting inhibitors based on ethylenediamine and chlorohydric acid phosphates. Readings of A.I. BULATOV, Materials of IV International scientific and practical conference. Crasnodar, 2020, pp. 126-128.
8. Puchina G.R., Ragulin V.V., Telin A.G., Alimbekova S.R., Bakhtizin R.N., Voloshin A.I., Dokichev V.A. Modern practice of salt deposition preventing and removing. *Neftegazovoe delo.* 2020, vol. 18, no. 2, pp. 72-80. DOI: 10.17122/ngdelo-2020-2-72-80.
9. Sultanova D.A., Mardashov D.V. Analysis of methods to enable anti-corrosion protection of downhole equipment. *XIX International scientific and practical conference "Modern trends in the development of science and technology":* Collection of scientific papers. Belgorod, 2016, pp. 132-135.
10. Tananykhin D.S., Maksyutin A.V., Sultanova D.A. Analysis of sand production forecasting models in the operation of poorly cemented reservoirs. *Modern problems of science and education.* 2015, no. 1-1. URL: http://www.science-education.ru/ru/article/view?id=19029
11. Sultanova D.A., Maksyutin A.V., Khusainov R.R. Experimental studies of the effectiveness of corrosion inhibitors for the protection of downhole equipment. International forum-competition of young scientists *"Problems of subsurface resources management":* Collection of scientific papers. St. Petersburg, 2013, pp. 58-59.
12. Elasheva O.M., Smirnova L.N. Effect of the corrosion inhibitor Soncor on salt precipitation in formation waters of the Yuzhno-Neprikovskoye field. *Eurasian Union of Scientists,* 2016, no. 3, pp. 80-83.
13. Sultanova D.A., Mardashov D.V., Khusainov R.R.. Investigation of the effect of scale inhibitors on the effectiveness of corrosion inhibitors in oil wells. *Scientific and technical journal "Oil Engineer",* 2016, no. 2, pp. 53-56.
14. Valekzhanin I.V., Ishmiyarov E.R., Presnyakov A.Y., Latypov O.A., Garifullin A.R., Voloshin A.I. Adsorption-desorption studies of a complex-acting oilfield reagent with the properties of a scaleand hydrate formation inhibitor. *Neftegazovoe delo.* 2020, vol. 18, no. 2, pp. 50-63. DOI: 10.17122/ngdelo-2020-2-

50-63.
15. Shangaraeva L.A., Petukhov A.V. Study of the adsorption-desorption properties of the composition to prevent scale deposits in downhole equipment. *Modern problems of science and education.* 2012, no. 6. URL: https://science-education.ru/ru/article/view?id=8007
16. Bikchantaeva N.V., Monakhova N.V., Aleshkina I.V. Investigation of the properties of a new salting inhibitor SNPCH-5312 (grades C and T). *Oil industry*. 2000, no. 11, pp. 39–40.

QEYRİ-ÜZVİ DUZ ÇÖKÜNTÜLƏRİNİN ARADAN QALDIRILMASI ÜÇÜN İNHİBİTORUN İŞLƏNİLMƏSİ VƏ TƏDQİQİ

X.İ. Həsənov, N.N. Xəlilov

"Neftqazelmitədqiqatlayihə" İnstitutu, SOCAR, Bakı, Azərbaycan
e-mail: x.qasanov58@gmail.com

Xülasə: *Neftayırma avadanlıqlarında və boru kəmərlərində duz çöküntülərinin aradan qaldırılması üçün inhibitorlaşmış xlorid turşusu, ES 9660A markalı dispersant, 4202-2B-30 markalı laprol və su əsasında yeni tərkibli duzçökmə inhibitorları işlənib hazırlanmışdır. Hazırlanmış tərkiblərin 20 ºC-də sıxlığı 1020-1050 kg/m^3, kinematik özlülüyü 30-40 mm^2/s, donma tempetaruru mənfi 5-15 ºC, hidorgen göstəricisi pH=2-3 təşkil edir. Duzçökmə inhibitorunun effektivliyi reagentin süni hazırlanmış mineral suyun ümumi həcmində kalsium kationlarını tutmaq qabiliyyətinə əsaslanan vahid metodika üzrə qiymətləndirilmişdir. Müəyyən edilmişdir ki, işlənmiş tərkiblər 50 mq/l sərfiyyatında müqayisədə daha yüksək qoruyucu effektə (76.3-85.6 %) malikdirlər nəinki 40 mq/l (73.1-83.2 %) və 30 mq/l (70.4-78.1 %) sərfiyyatında. Tərkibində 10 % 4202-2B-30 laprol olan kompozisiyalar daha yüksək qoruyucu effekt göstərirlər.*

Açar sözlər: *duzçökmə inhibitoru,inhibitirlaşmış xlorid turşusu,səthi aktiv maddə, inhibitorlaşma effektivliyi, kalsium sulfat, aktiv maddə.*

РАЗРАБОТКА И ИССЛЕДОВАНИЕ ИНГИБИТОРА ОТЛОЖЕНИЯ НЕОРГАНИЧЕСКИХ СОЛЕЙ

Х.И. Гасанов, Н.Н. Халилов

НИПИ «Нефтегаз», SOCAR, Баку, Азербайджан
AZ 1012, Баку, ул. Зардаби, 88; e-mail: x.qasanov58@gmail.com

Аннотация: *Разработаны составы для ингибирования отложений солей, проявляющихся на нефтеперерабатывающих оборудованиях и трубопроводах, на основе ингибированной соляной кислоты, дисперсанта ЕС 9660А, лапрола 4202-2Б-30 и воды. Плотность приготовленных составов при 20 ºС составляет 1020-1050 кг/м^3, кинематическая вязкость 30-40 мм^2/с, температура застывания минус 5-15 ºС, показатель водорода pH =2-3. Эффективность ингибирования солеотложения оценивалась по единой методике, основанной на способности реагента удерживать катионы кальция и магния в объеме модельных растворов, имитирующих пластовые воды. Установлено, что наибольший защитный эффект (76.3-85.6 %) приготовленных составов наблюдается при расходе*

ингибитора 50 мг/л. Очень высокие результаты по защитному эффекту проявляют составы, в которых массовая доля лапрола 4202-2Б-30 составляет 10 %.

Ключевые слова: *ингибитор солеотложения, ингибированная соляная кислота, поверхностно-активное вещество, эффективность ингибирования, сульфат кальция, активное вещество.*