

## Prediction of Corrosion Resistance of the Casing Bottom Structure Caused by $H_2S$ - $CO_2$ Affect in Highly Mineralized Formation Fluids of Iraq Oil Deposits

*D. F. Donskyi<sup>1</sup>, S. V. Nesterenko<sup>2</sup>, Ameer Neamah<sup>1</sup>, A. G. Tulska<sup>2\*</sup>, K. M. Dihtenko<sup>3</sup>*

<sup>1</sup> *Department of oil, gas and gas condensate production, National technical "Kharkiv polytechnic institute", Kharkiv, Ukraine*

<sup>2</sup> *Department of chemistry and integrated technologies, Kharkiv National Academy of Municipal Economy", Kharkiv, Ukraine*

<sup>3</sup> *UkrNDIGas, Gymnazichna embankment 20, Kharkiv, Ukraine*

Received July 6, 2021; Accepted January 14, 2022

---

### Abstract

The main reason of corrosion destruction of casing surface has been considered. Based on gravimetric, potentiometric and optical studies using mathematical planning of the experiment, the influence of various factors on the corrosion rate has been studied. Model of regression for different types of steel are compared and the role of inhibition in this process has been analyzed.

**Keywords:** *Corrosion; Corrosion rate; Hydrogen sulfide; Carbon monoxide; Casing; Regression.*

---

## 1. Introduction

Analysis of literature [1-6] confirms that reliability of well fastening has become an essential factor as the drilling depth increases, geological and technical conditions become more complex and part of drilling of inclined wells raises in the total volume of drilling. The main causes of problems and accidents in the process of fixing oil and gas wells were studied, the conditions of leakage of threaded connections of casing were investigated. Also, a significant role should be given to patents devoted to this area. They provide devices, methods and a variety of connections to improve the reliability of wells. These problems are characterized and solved during the years of well operation. The analysis of statistical data shows that the elimination of casing damage takes about 12% of the total emergency time, and therefore the improvement of casing design techniques for wells is relevant and requires comprehensive study.

Secondary oil production in southern Iraq with the use of water injection in many fields raises a problem - when oil is extracted from oil wells operated by Mishrif reservoirs, oil is extracted with a large amount of pumped water.

## 2. Previous research analysis

One of the possible causes of this problem is that the Mishrif Formation consists of hydrophobic carbonate ore rocks and is subject to strong dissolution, therefore, high inhomogeneous permeability zones are formed. Considering this, the water is distributed unevenly and the water-oil contact (WPC) rises unevenly along the entire length of the field [7-13].

Oil fields of Iraq are multilayered. This obstacle is the reason of poor cementing in the construction of wells, which occurs mainly with the use of Portland cement brand G. The presence of hydrogen sulfide and carbon dioxide in reservoir water creates conditions for intensive destruction of unprotected sections of casing, which leads to their premature decommissioning and can have adverse environmental consequences.

The methodology of solving this problem is the following. First, it is necessary to assess the fracture factors acting on the system within the field. These can be: temperature in the range

from 313 to 373 K; mineralization of formation water, namely, the content of chloride ions, in the range from 50 to 150 g/dm<sup>3</sup>, as well as the concentration of the active components H<sub>2</sub>S and CO<sub>2</sub>. It is proposed to consider the system of steel surface-cement coating as the only one that acquires its properties after hardening of the cement and the formation of a layer of cement stone.

This problem can be solved in different ways. First, we need to strengthen the stability of column by applying new types of steel - austenitic-ferritic, which have higher resistance to fracture in a highly mineralized environment containing highly active corrosive components H<sub>2</sub>S and CO<sub>2</sub>, and second, we need to strengthen the protective effect of cement layer with inhibitors.

Currently, a significant amount of information has been accumulated on the effect of hydrogen sulfide on the corrosion of carbon steels, their flooding and mechanical properties under operating conditions [14-30]. However, in order to establish the operability, to predict the lifetime of metal structures of oil and gas equipment and prevent accidents, it is necessary to study the behavior of relevant materials under operational conditions. However, it should be considered that these conditions (temperature, pressure, composition of the environment) in the development of deposits are not stable, and therefore it is necessary to study the influence of these factors, as well as external static and dynamic loads on corrosion and corrosion-mechanical behavior construction materials [16-17].

The form of brittle fracture under the action of hydrogen sulfide corrosion is associated with increased absorption of hydrogen atoms in pipeline steel, while the local tendency to point corrosion of metals in acidic conditions is closely related to thermodynamics, kinetics and nature of formed iron sulfide films [18-19]. Corrosion damage due to exposure to wet hydrogen sulfide (H<sub>2</sub>S) pipelines can be grouped into four main categories: 1) Hydrogen cracking, 2) Stress corrosion cracking (SCC) and hydrogen sulfide cracking (SSCC), 3) Local spot corrosion, 4) Other damage associated with hydrogen sulfide corrosion conditions containing other acid salts, chlorides, etc. [31-34].

Local fractures occur due to the presence of acidic anions (eg, chlorides), external influences during installation, accumulation of internal stresses in solid corrosion films, impact of solid particles during operation, as well as due to the heterogeneity of the fabricated microstructural phase [35-37] and others.

Halides, and especially chlorides, are the most aggressive anions that promote the initiation of pitting, penetrating into the local cavities created by the destruction of passive oxide films [35, 37]. The mechanism of film destruction seems to be the most probable, as it may be clearly related to the accumulation of mechanical stress [37].

Dry and pure CO<sub>2</sub> usually does not cause corrosion, but is soluble in aqueous phase with formation of low-concentrated carbon dioxide. CO<sub>2</sub> gas is usually present in oil and gas tanks and is easily soluble in liquids extracted from oil fields [14]. Having been dissolved in underground water, gaseous CO<sub>2</sub> turns to H<sub>2</sub>CO<sub>3</sub> which is a strong corrosion activator [14].

Modern austenitic-ferritic steels due to special corrosion and mechanical properties are promising for use in many areas of chemical, petrochemical and oil and gas industries, in marine construction and in seawater desalination. The increase in the production of austenitic-ferritic steels of the third generation refers to the 70-80 years of the XX century. Currently, leading metallurgical firms in various countries (Germany, France, Great Britain, the United States, Sweden, etc.) offer low-carbon nitrogen-containing steels [38].

### 3. Aim and scope

The aim of the current research is to study the corrosion resistance of modern austenitic-ferritic steel (AKS AISI 304, Super DKS-SAF 2507 by Sandvik) in formation waters of Iraqi oil fields in comparison to steel K-55 (the closest analogue in Ukraine - steel 45) by measuring corrosion rate. Another one important direction is to study mechanism of local corrosion of these types of steel in highly mineralized reservoir water of oil fields in presence of hydrogen sulfide and carbon gas by studying the dynamics of the process in metallographic studies.

Corrosion-resistant austenitic-ferritic duplex corrosion-resistant steels (DKS) consist of two main phases - austenite (A) and ferrite (F) in approximately equal amounts (at least 30% each). Both of these phases are corrosion-resistant due to their high chromium content. Advantages of DKS over austenitic corrosion-resistant steels (AKS) - twice higher durability in comparison with austenitic, insensitivity to corrosion cracking (KR) and intercrystalline corrosion (MKK).

### 3.1. Description of materials and methods of the experiment

The chemical composition of the studied materials and formation water are given in Tables 1 and 2. Corrosion rate was studied by potentiometric, gravimetric and optical methods [38].

Table 1. Chemical content of the researched types of steel

Type of steel	C	S	P	Cr	Ni	Mo	N	PRI *
SAF-2507	0.02	0.01	0.03	25	7	4	0.27	43
AISI 304	0.08	0.03	0.045	19	9.3	-	-	-
Steel 45	0.1	0.02	0.035	13.3	1.2	2.4	-	-
Steel K55	0.12	0.004	0.02	-	-	-	0.01	-

PRI\* - pitting resistance index

Table 2. Characteristics of formation water

Density, g/dm <sup>3</sup>	pH	Concentration of minerals, g/dm <sup>3</sup>	Chlorides concentration, g/dm <sup>3</sup>
1 147.0	6.1	202.0	125.0

## 4. Results and discussion

Table 3. The corrosion rate of the investigated steels in formation water at a temperature of 80° C is calculated from cyclic voltammograms

Type of steel	Corrosion rate (g/(m <sup>2</sup> * h))		
	Experiment 1 Formation water	Experiment 2 Formation water, saturated with CO <sub>2</sub>	Experiment 3 Formation water, saturated with H <sub>2</sub> S
SAF-2507	0,42	0,55	0,57*
AISI 304	0,68*	0,82*	0,98*
Steel 45	6,27*	8,88*	9,61*
Steel K55	7,21*	9,23*	10,65*

\*intensive pitting

Corrosion processes on SAF-2507 steel proceed evenly and ulcerative corrosion was not detected in contrast to steels Steel 45, K-55 and AISI-304. Types of destruction of steel during gravimetric tests in the formation water of one of the oil fields in Iraq are shown in Fig. 1.

Steel SAF-2507 has significant resistance to ulcerative corrosion due to the fine-grained austenitic-ferritic structure, as well as because it contains 4-6% molybdenum in its composition. This is also evidenced by the results of metallographic analysis of metal samples (Fig. 1). The structure of the metal SAF-2507 is austenitic with the available liquation strips in the middle of the sheet, which indicates the formation of secondary phases in the metal [39].

Analysis of the data in Table 4 shows that the corrosion rate of steel K55 (Ukrainian analogue-steel 45) in formation water increases with increasing temperature, especially in the presence of carbon dioxide and hydrogen sulfide. Corrosion is uneven ulcerative in nature. Corrosion of AISI 304 steel is ulcerative.

In general, the corrosion rate is a function of these factors, which can be considered independent (1):

$$Y=f(x_1, x_2, x_3, x_4) \quad (1)$$

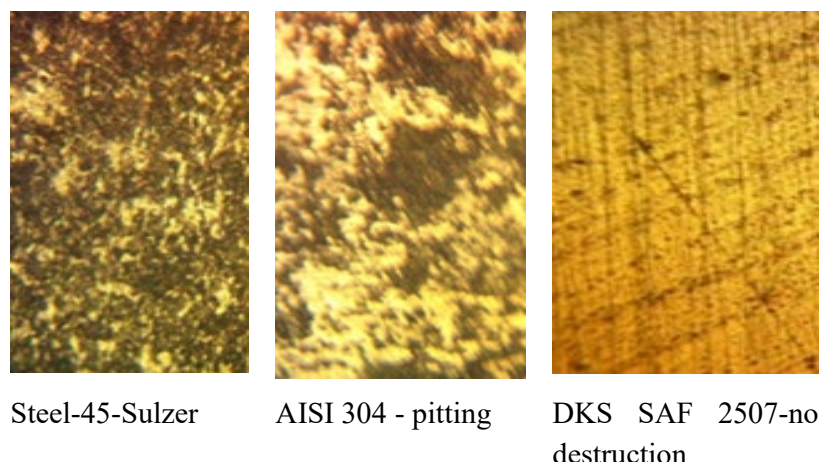


Figure 1. Metallographic studies of steel samples after testing in formation water; zoom x 200

The corrosion rate  $V$  ( $\text{g}/(\text{m}^2 \cdot \text{h})$ ) was chosen as the objective function. Experiments for 4 variants were carried out in a single factor space with intervals of variation, which are given in the plan – matrix (Table 4) using Central-compositional (rotatable) plan of the second order. Processing of experimental results and analysis of regression model was carried out using the module "Experimental planning" of the statistical program Statgraphics Plus [40-41].

Table 4. Experiment factors

Factor	Factor's code	Units	Factors levels				
			-2	-1	0	+1	+2
Chlorides concentration	A	$\text{g}/\text{dm}^3$	20	40	80	120	160
Temperature	B	$^{\circ}\text{C}$	50	65	80	95	110
$\text{CO}_2$ content	C	%	0,1	1,1	2,1	3,1	4,1
$\text{H}_2\text{S}$ content	D	%	0,02	0,62	1,22	1,82	2,42

As a result of the analysis of the received regression models (Fig. 2) the accurate tendency in an estimation of significance of factors of acceleration of corrosion rate for investigated steels is observed. For both steels, the temperature factor is the most important. Unlike SAF-2507, the corrosion rate for steel 45 depends on all selected factors and some of their combinations (Fig. 2 a). The application of a cement coating modified with a corrosion inhibitor significantly reduces the number of significant factors for surface corrosion for this steel (Fig. 2 b). This confirms the existence of a certain protective effect of the layer of modified cement. The corrosion rate for SAF-2507 steel under concrete protection depends only on the temperature and a combination of factors determined by the content of hydrogen sulfide and carbon dioxide.

Figure 2. Corrosion rates of different steel samples; a) without cement coating

A)
SAF-2507
$V_1 = 0,155 + 0,0629583 \cdot \text{Factor}_B + 0,0267917 \cdot \text{Factor}_D + 0,0196875 \cdot \text{Factor}_C \cdot \text{Factor}_D$
Steel 45
$V_2 = 1,915 + 0,4425 \cdot \text{Factor}_A + 2,70625 \cdot \text{Factor}_B + 0,598333 \cdot \text{Factor}_C + 0,646667 \cdot \text{Factor}_D + 0,51875 \cdot \text{Factor}_A \cdot \text{Factor}_B + 1,02094 \cdot \text{Factor}_B^2 + 0,79625 \cdot \text{Factor}_B \cdot \text{Factor}_C + 0,78125 \cdot \text{Factor}_B \cdot \text{Factor}_D$

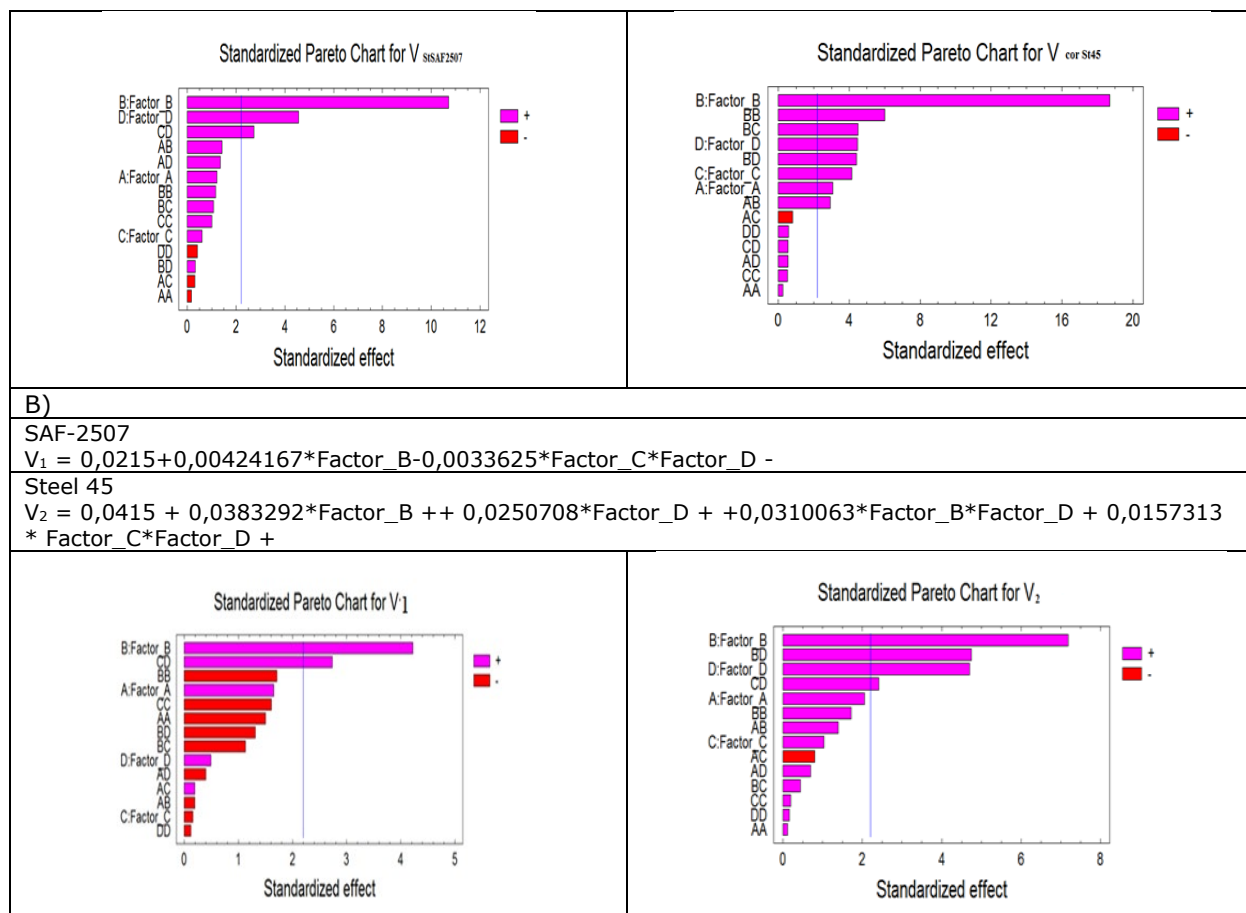


Figure 2. Corrosion rates of different steel samples; a) without cement coating; b) under a layer of modified cement coating

## 5. Conclusions

The current research and mathematical methods of analysis provided the estimation of influence of various corrosion factors on destruction intensity for various samples of steel. Also, the regression equations have been received. Analysis of the obtained models showed that the application of modified corrosion inhibitor concrete coating significantly reduces the number of factors affecting the rate of corrosion of steel. Austenitic-ferritic steel SAF-2507 provides higher stability in aggressive environment that simulates the formation waters of Iraq's oil fields.

## References

- [1] Moisishin VM. Obsadni trubitaïkh Z'ednannya: analiz sortamentu, otsinka napruzhenno-deformovanogo stanu, Burinnya naftovikh i gazovikh sverdlovin., Naukovii visnik IFNTUNG, 2010; 1(23): 58-67.
- [2] Kiselev AI. Sposoby i materialy dlya germetizatsii i vostanovleniya germetichnosti soedinitel'nykh uzlov obsadnykh kolonn. Ser. Burenie, 1987 ;48 p.
- [3] Kotskulich YA. Zakinchuvannya sverdlovin:Interpres LTD, 2009; 366 s.
- [4] Kotskulich YA. Stan kriplennya naftogazovikh sverdlovin i shlyakhi iogo pokrashchennya. Naukovii visnik IFNTUNG, 2005; 2: 41-44.
- [5] Kotskulich YA. Stan i perspektivi pidvishchennya nadiinosti kriplennya sverdlovin: Naftova i gazova promislovist', 2007; 5: 22-24.

- [6] Kotskulich YA. Rezervy povysheniya nadezhnosti raboty obsadnykh kolonn v neftnykh i gazovykh skvazhinakh; Tekhn., tekhnologiya i organizatsiya geol.-razved. Rabot; MGP Geoinformmark, 1991.
- [7] Beydoun ZR. Geologiya i potentsial'nye zapasy uglevodorodov Araviiskoi plity v svete tektoniki plit: Geologicheskie issledovaniya, 1991:33;77 p.
- [8] Sharland PR, Archer R, Casey DM, Davies RB, Hall SH, Heward AP, Horbury AD, Simmons MD. Stratigrafiya razreza Araviiskoi plit: «GeOAraviYA», Spetsial'nyi vypusk, № 2. Bakhrein: Galf Petro-Link, 2001. 371 s.
- [9] Konert G. Al-Afifi AM, Al-Hajri SA. Stratigrafiya paleozoya i lokalizatsiya uglevodorodov Araviiskoi plity, 2001; 6(3): 407-442.
- [10] Al-Naqib KM. Geologiya Araviiskogo poluostrova: Yuzhnyi Irak. Geologicheskaya sluzhba SSHA, 1967: 54 p.
- [11] Murris RJ. Srednii Vostok: Stratigraficheskaya ehvolyutsiya i lokalizatsiya nefti: Byulleten' Amerikanskoi assotsiatsii geologov-neftyanikov, 1980; 64: 597-618.
- [12] Al-Husseini MI. Stratigrafiya yurskikh otlozhenii zapadnoi i vostochnoi chasti Araviiskogo zaliva . GeOAraviYA. 1997; 2 (4): 361-382.
- [13] Makhavi MM, Takher AK, Zaibel' KHG, Sidnev AB. Obshchaya skhema tektonicheskoi ehvolyutsii Araviiskoi plity v fanerozoie. Visnik Natsional'nogo tekhnichnogo universitetu «KHPI». 2020; 2(4) 2020: 35-37.
- [14] Kermani BM and Morshed A. Carbon dioxide corrosion in oil and gas production: A compendium. Corrosion. 2003; 08: 659-683.
- [15] Kermani MB and Harrop D. The impact of corrosion on oil and gas industry. SPE Production & Operations. 1996; 11 (3): 186-190.
- [16] Ramirez FA, Hill R, and Martinez S. Material assessment for souring subsea systems. Offshore Technology Conference, Houston, Texas, USA, 2010
- [17] Zeng D, Huang L, Gu T, Huo S, Lin Y, Hongjun Z, and Yin H. Evaluation and selection of OCTG and gathering lines for high sour gas fields. International Oil and Gas Conference and Exhibition in China, Beijing, China: Society of Petroleum Engineers, 2010.
- [18] Moosavi AN, Rumash K, and Kadri M. Material selection for downhole sour environment. Abu Dhabi International Petroleum Exhibition and Conference, Abu Dhabi, UAE: Society of Petroleum Engineers, 2008.
- [19] Kermani MB, and MacCuish RG. Materials assessment for sour service applications", SPE Annual Technical Conference and Exhibition, New Orleans, Louisiana: 1990.
- [20] Radkevich OI, Pokhmurskii VI. Vliyanie serovodoroda na rabotosposobnost' materialov i oborudovaniya gazodobyvayushchikh promyshlennostei . Fiz.-khim. mekhanika materialov. 2001; 37 (2): 157-168.
- [21] Saakiyan LS, Efremov AP. Zashchita neftegazopromyslovogo oborudovaniya ot korrozii. Nedra, 1982. – 227 p.
- [22] Martinyuk TA, Chernova OT. Proekt ekspluatatsii gazovogo rodovishcha z vmistom sirkovodnevikh domishok. Naukovii visnik IFNTUNG. 2012; 2(32)
- [23] Kolotyrkin YA. Pittingovaya korroziya metallov. Khimicheskaya promyshlennost. 1963; 3: 38-46.
- [24] Podobav NN, Atanasyan TK, Getmanskii MD, Kozlov AN. Vliyanie nekotorykh azotsoderzhashchikh ingibitorov na lokal'nuyu korroziyu v khloridnosul'fidnykh rastvorakh. Zashchita metallov. 1989; 25(4) : 683-686
- [25] Shreider AB. Ehlektrokhimicheskaya serovodorodnaya korroziya stali. Zashchita metallov, 1990; 26(2): 179-190.
- [26] Gonik AA. Korroziya neftepromyslovogo oborudovaniya i mery ee preduprezhdeniya. – M.: Nedra, 1976. – 192 s.
- [27] Iofa ZA. O mekhanizme deistviya serovodoroda i ingibitorov na korroziyu zheleza v kislykh rastvorakh. Zashchita metallov. 1980; 16(3): 295-300.
- [28] Otsenka stoikosti nizkouglerodistykh trubnykh stali pri korrozii v usloviyakh teplotrass . Zashchita metallov. 1999; 35 (1): p. 8-13.



- [29] Getmanskii MD, Rozhdestvenskii YUG., Khudyakova LP, Nizamov KP. Lokal'naya korroziya neftegazopromyslovogo oborudovaniya v serovodorodsoderzhashchikh mineralizovannykh sredakh. Korroziya i zashchita v neftegazovoi promyshlennosti". 1981. 11: 2–10.
- [30] Kete G. Korroziya metallov. Fiziko-khimicheskie printsipy i aktual'nye problemy. Morskaya i neftyanaya geologiya. 1992; 9: 474-485.
- [31] Kermani B. Materials optimization for oil and gas sour production. Corrosion, paper no. 156, Orlando, FL.: NACE International, Houston, Texas, 2000.
- [32] Ramirez FA, Hill R, and Martinez S. Material assessment for souring subsea systems. Offshore Technology Conference, Houston, Texas, USA, 2010.
- [33] Kermani B, Perez TE, Morales C, Turconi GL, and Gonzales JC. Materials optimisation in hydrocarbon production. Corrosion, paper no. 111, Houston, TX: NACE International, 2005.
- [34] Sun H, Blumer D, and Davis J. Pit propagation of carbon steel in sour conditions. Corrosion, paper no. 282, San Antonio, TX: NACE International, 2010.
- [35] Baboian R. Corrosion Tests And Standards: Application And Interpretation. 2005: Astm International.
- [36] Zhu Z, Tajallipour N, Teevens PJ, Xue H, and Cheng FYF. A mechanistic model for predicting localized-pitting corrosion in a brine water-CO<sub>2</sub> system. Corrosion, paper no. 256, Houston, TX:NACE International, 2011.
- [37] Garber DJD, Knierim DK, Acuna MJ, and Deokar MKC. Modelling pitting corrosion in a CO<sub>2</sub> system containing bacteria. Corrosion, paper no. 545, New Orleans, LA: NACE International, 2008.
- [38] Nemakh A, Donskyi DF, Nesterenko SV. Vivchennya vplivu CO<sub>2</sub>, H<sub>2</sub>S i temperaturi plastovoï vodi naftovogo rodovishcha na rozvitok pitingovoï korozii. Komunal'ne gospodarstvo mist, 2019; 3(149): 58–68.
- [39] Sereda BP, Bannikov LP, Nesterenko SV, Kruglyak IV. Poverkhneve zmitsnennya materialiv pratsyuyuchikh v umovakh kompleksnogo vplivu agresivnikh rechovin. Kam'yans'ke: DDTU, 2019; 173 s.
- [40] Bilets'kii VS, Smirnov VO. Modelyuvannya protsesiv zbagachennya korisnikh kopalin. Donets'k: Sdnii vidavnychii dim, 2013; 304 p.
- [41] Sergeev PV, Bilets'kii VS. Kompyuterne modelyuvannya protsesiv pererobki korisnikh kopalin. Praktikum\_Mariupol':Skhidnii vidavnychii dim. 2016; 119 p.

---

*To whom correspondence should be addressed: Dr. A. G. Tulska, Department of oil, gas and gas condensate production, National technical "Kharkiv polytechnic institute", Kharkiv, Ukraine, E-mail: [fuel.khpi@gmail.com](mailto:fuel.khpi@gmail.com)*