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STUDY OF VACUUM BLOCK CORROSION STATE IN VISBREAKING UNIT JSC "GAZPROM NEFTEKHIM SALAVAT"

ИССЛЕДОВАНИЕ КОРРОЗИОННОГО СОСТОЯНИЯ ВАКУУМНОГО БЛОКА УСТАНОВКИ ВИСБРЕКИНГ НПЗ ОАО «ГАЗПРОМ НЕФТЕХИМ САЛАВАТ»

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Abstract. The paper presents an analysis of the corrosion state the vacuum block of visbreaking unit JSC "Gazprom neftekhimSalavat", provided on the monitoring data during 2012 – 2013 years. Examined steel grades which used at the manufacturing of basic technological equipment of the vacuum unit, (distillation column, ejectors, heat exchangers, tanks, pipelines) and corrosion resistance of them. Given the brief characteristic of technological parameters, analyzed the possible areas of corrosion damage. Results of the analysis of the condensation water from reflux drums and heat exchangers in terms of pH, dissolved iron mass fraction, mass fraction of chlorides. It is shown that the pH value is in the range of 5.5-8.8 units, and the maximum content of total dissolved iron is 8.9 mg/dm^3. This article also shows the results of measurement of corrosion rate of the selected aqueous condensate in a laboratory by electrochemical and gravimetric methods. Results were within 0.15-0.2 mm/year.

The paper presents survey results of process equipment during the renovation of a visbreaking unit in 2013 – ejectors, barometric and water seal vessels, heat exchangers of 1-4 condensation stages - on presence of traces corrosion and corrosion damage. Based on analysis it was concluded that the state of the equipment is satisfactory, which was confirmed by special tests.

Further work presents an analysis of data measuring the thickness of the vacuum unit metal pipe during the 2012 and 2013, according to which the pipe sections in some places have the corrosion rate up to 0.5-3.0 mm/year. Therefore we recommended for the use of pipelines from corrosion-resistant steel in the areas most exposed to corrosion.

For integrated and lasting solution to the question of corrosion on the vacuum unit recommended the introduction of chemical engineering corrosion protection with using of reagents.

Аннотация. В работе представлен анализ коррозийного состояния вакуумного блока установки висбрекинг ОАО «Газпром нефтехим Салават», проведенный на основе данных мониторинга 2012-2013г. Рассмотрены марки стали, используемые при изготовлении основного технологического оборудования вакуумного блока (ректификационная колонна, эжектора, теплообменники, емкости, трубопроводы), и их коррозионная стойкость. Дана краткая характеристика технологических параметров установки, проанализированы возможные зоны коррозионного поражения. Приведены результаты анализа водного конденсата из холодильников и рефлюксных емкостей по показателям pH, массовая доля растворенного железа, массовая доля хлоридов. Показано, что водородный показатель находится в диапазоне 5,5-8,8 ед., а максимальное содержание общего растворенного железа составляет 8,9 мг/дм^3. В статье также даны

результаты измерений скорости коррозии, отобранного в лабораторных условиях с установки водного конденсата электрохимическим и гравиметрическими способами, которая составила величину порядка 0,15-0,2 мм/год.

В статье отражены результаты обследования технологического оборудования в период ремонта установки висбрекинг в 2013 г – эжекторов, барометрической и гидрозатворной емкостей, холодильников 1-4 ступеней конденсации – на наличие следов коррозии и коррозионных повреждений. По результатам обследования сделан вывод, что состояние оборудования удовлетворительное, что также было подтверждено специальными испытаниями.

Далее в работе представлен анализ данных замеров толщины металла трубопроводов вакуумного блока установки в 2012 и 2013 гг., согласно которым были обнаружены участки труб, где скорость коррозии составляет 0,5-3,0 мм/год. В связи с этим даны рекомендации по применению трубопроводов из коррозионностойких марок стали на участках, наиболее подверженных коррозии.

С целью комплексного и долговременного решения вопроса коррозии на вакуумном блоке рекомендуется внедрение элементов химико-технологической защиты от коррозии с применением соответствующих реагентов.

Key words: vacuum unit, corrosion, visbreaking, inspection, corrosion condition, corrosion monitoring, chemical-protection technology.

Ключевые слова: вакуумный блок, коррозия, висбрекинг, обследование, коррозионное состояние, коррозионный мониторинг, химико-технологическая защита.

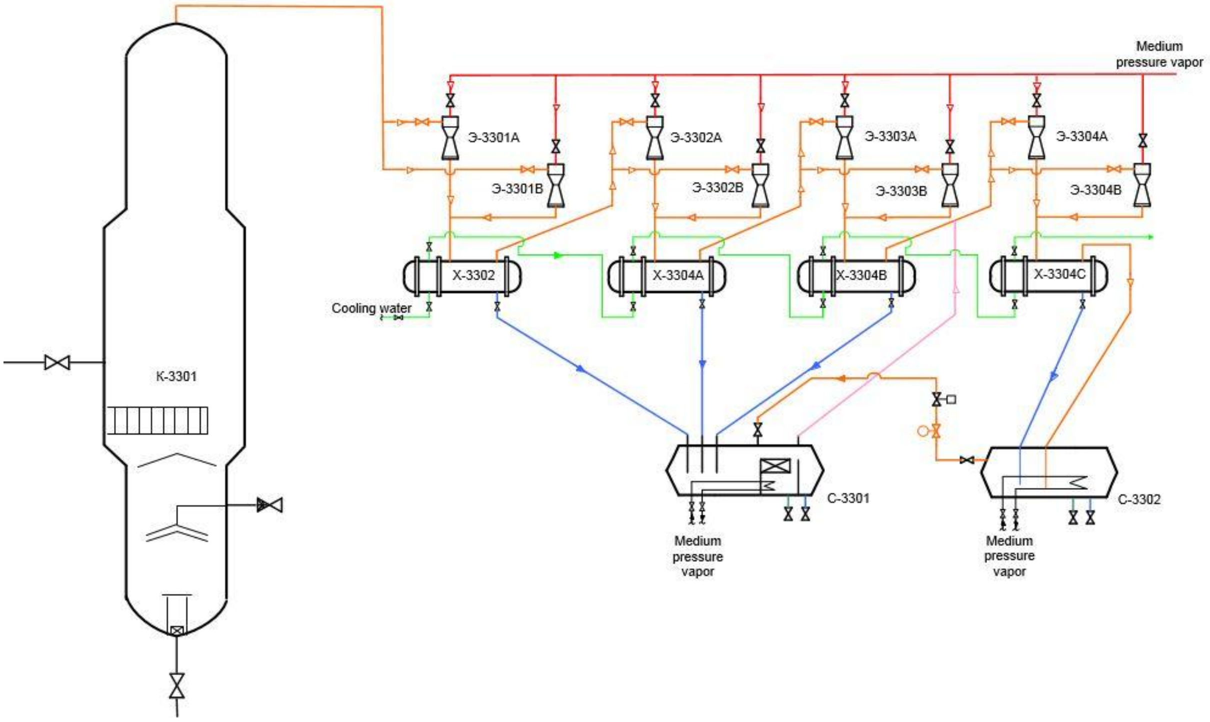
Visbreaking unit of JSC "Gazprom neftekhimSalavat" was commissioned in 2008. Basic installation project designed by the Shell Global Solutions Int, Holland. Detailed design completed by company “Kedr-89”

The main purpose of visbreaking process - reducing the viscosity of raw materials - tar from vacuum distillation units, by to the thermal cracking process under mild conditions. Viscosity reduction reduces the amount of high-quality distillates to be added to the residue visbreaking , for a commodity product - fuel oil M-100. Rated capacity of visbreaking unit of JSC «Gazprom neftekhimSalavat» by tar is 1500 tons per year. Entering these settings allowed increasing oil refining in plant and beginning to producing commercial fuel oil from refinery residues without involving light and gas oil fractions.

Vacuum block of visbreaking unit is presented by column K-3301, which operates as a "dry" distillation, without steam supplying.

Residual pressure at the top of the column 1.2 – 3.0 kPa, temperature 80-85 ° C. Vacuum supported by four-stage steam jet pump, each of pump includes two stage ejector. In ejectors fed medium pressure steam, to condense water, condensers used refrigerators. Condensed oil and acidic water coming into the barometric and water seal vessels C-3301 and C-3302, respectively, which are separated and removed them from the unit.

During the designing and construction of the unit were used different grades of metals (Table 1).Column, ejectors and reflux vessels are made of alloyed stainless steels, heat exchangers of low-alloy and piping of conventional steels. Consequently, special attention is necessary to monitoring pipelines and heat exchangers.



Picture1. Block diagram of the vacuum block of the visbreaking unit:

К-3301 – vacuum column; Э-3301A/B - Э-3304 A/B – ejectors; X-3302, X-3304A/B/C – coolers/condensers; C-3301 – barometric vessel ;C-3302 - water seal vessel

Table 1. Characteristics of steels vacuum unit equipment

№	Processequipment	Steelgrade	Characteristics of the steel grade [5]
1	Vacuum column К-3301	09G2C+ 08X13	Double-layer corrosion-resistant sheets cladding layer of corrosion-resistant steel.
2	Vacuum 1-4 stages of ejection Э-3301A/B - Э-3304 A/B	09G2C-4, 10G2	Coating of structural steel alloy.
3	Barometric vessel (1 stage of condensation) - C-3301 water seal vessel (2 stage of condensation) - C-3302	09G2C-6 + 12X18H10T	Double-layer corrosion-resistant sheets cladding layer of corrosion-resistant cryogenic steel.
5	Steam condensers, after vacuum ejectors (1-4 stage of condensation) X-3302 A/B, X-3304A/B/C	09G2C-6, steel 20	Lowalloystructuralsteel
6	Pipelines	steel 20	Structuralcarbonsteel

During 2012-2013 were made random monitoring of quality indicators of acidic water from reflux drum and heat exchangers 3301 X-3302 A/B and X-3304 A/B/C. According to the analysis of water condensate from the heat exchangers, made in May 2012, the pH value was in the range 5,5-8,8 units, and the content of total dissolved iron does not exceed 2,1 mg/dm^3 (Table 2).

Table 2. Results of the analysis of water condensate from coolers X-3302A, X-3304-A/B/C

Selection place	pH	Mass concentration, mg/dm^3			
		Cl ions	Sulfide ions	the amount of dissolved and undissolved forms of Fe	Fe, totaldissolved
28.05.2012					
X-3302A	5,7	0,07	11,2	8,3	1,2
X-3304A	8,3	0,1	48	1,2	0,3
X-3304B	6,5	0,03	46,4	1,5	2,1
X-3304C	6,6	0,08	36	18,8	1,2
30.05.2012					
X-3302A	8,8	0,11	7,6	40,3	1,6
X-3304A	6,6	0,04	92	2,8	0,2
X-3304B	6,7	0,05	104	0,9	0,2
X-3304C	5,5	0,17	57,6	13,3	2,1
31.05.2012					
X-3302A	8,2	4,95	0,9	4,2	0,1
X-3304A	7,5	6	22,4	0,2	0,03
X-3304B	7,7	8,81	23,3	5,7	1,4
X-3304C	7,6	7,37	16,8	0,07	0,07

Analyzed data of water from the vessel C-3301 and the same heat exchangers in April-May 2013 showed that pH = 5.48-8.10 units, and total dissolved Fewere within 1.4-8.9 mg/dm^3 (Table 3,4).

Table 3. Results of the analysis of water reflux drum C-3301 (April 2013)

Indicator	Vessel C-3301		
	3.04.13	10.04.13	17.04.13
pH, units	7,22	6,35	6,56
Mass concentration of total dissolved Fe, mg/dm^3	8,9	6,8	4,9

Table 4. Analysis results of water condensate from the heat exchangers 3302 X A/B and X-3304 A/B/C (April-June 2013)

Indicator	X-3302 A		X-3304B		X-3304C	
	23.04.13	20.06.13	20.06.13	03.07.13	20.06.13	03.07.13
pH, unit	8,10	7,11	5,70	6,06	5,48	5,80
Mass concentration of total dissolved Fe, mg/dm^3	1,4	1,5	1,9	2,6	2,4	2,3

Thus, the pH and the dissolved total Fe of the water reflux from the vessel C-3301, and the condensate from the heat exchangers X-3302 A/B, X-3304 A/B/C have values at which the corrosion processes occur with low speed, however, boundary values of pH = 5.5 units and concentration of Fe ions equal to 8.9 mg/dm^3. It alerts, especially after given the fact that the control of these parameters is not included in analytical control chart of visbreaking unit.

Next were done laboratory measurements of corrosion rate by gravimetric method according to GOST 9.506-87, which is determines the mass losses of metal samples during their staying in the test environment and then calculating the rate of corrosion.

As the investigated medium we used water from the vessel C-3301, metal plates material is steel St3sp. Corrosion rate measured by gravimetrical method in the anoxic medium was approximately 0.15 mm/year.

At the next stage of research, we measure corrosion rate by the electrochemical method using corrosion gage Monicor-2M with a two-electrode sensor electrodes made of polarization resistance of steel grade St3sp in oxygen-free environment. Figure 2 shows the curve of the corrosion rate, taken in the aqueous condensate, in 03.04.2013, out of the vessel C-3301.

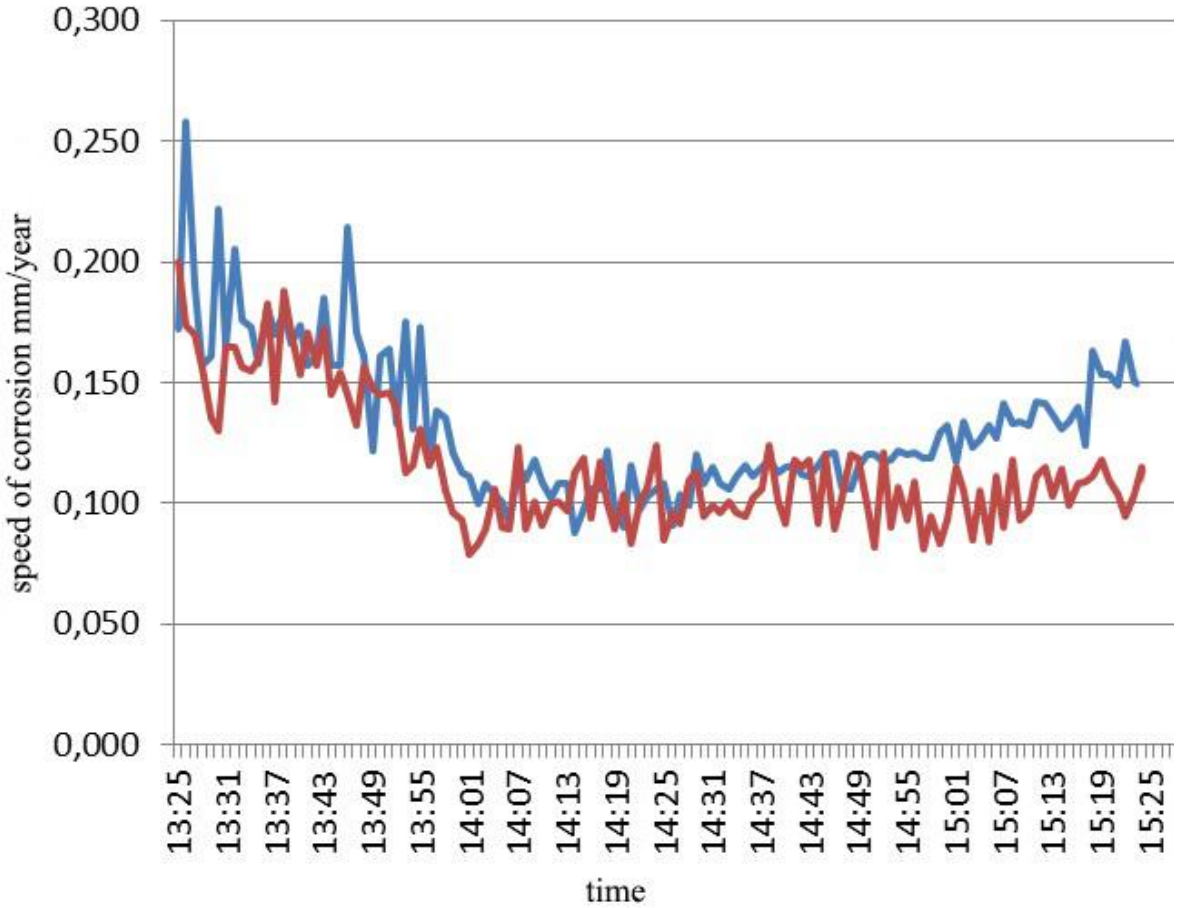


Figure 2. Corrosion rate curve in the water from the vessel C-3301. 03.04.2013.(the two parallel measurements)

Figure 2 shows that the corrosion rate in water from the vessel C-3301 from 03.04.2013 not exceed an average of 0.15 mm/year. Measured values are in good correlation with gravimetric measurements.

Further, were measured the corrosion rate from condensate out of heat exchanger X-3302A in 23.04.2013 by the electrochemical method, the same way. In this unit we would expect most corrosively environment as it refrigerator first condensation stage. The measurement results showed that the corrosion rate of a curve similar to Figure 2, and the corrosion rate within 0.15 mm/year.

The resulting corrosion rates in good agreement with the measured values of pH and the total content of dissolved iron in these samples.

In September and October of 2013 was done planned repairsof visbreaking unit, during which was performed and examined the basic technological equipment, the most likely to corrode.

Inspection ejectors and vessels C-3301, C-3302 showed the absence of corrosion on the internal surfaces of equipment. Then was inspected condensation heat exchangers equipment for presence of corrosion and deposits. On the surface of inside bundles X-3302A/B, X-3304A a thin layer of corrosion has been detected; the deposits are present in minor amounts. Bundles on the heat exchanger X-3304B contained more deposits. A significant amount of deposits observed when were inspected bundles in X-3304C heat exchanger, with no appreciable corrosion damage. During the examination of condensation-cooling vacuum equipment reads as follows:

- Corrosion and corrosion damage on the surface of the bundles heat exchanger were not observed;

- From the first to the fourth stage of ejection, an increasing of the deposits on the respective heat exchanger bundles.

- Ejectors and inner surfaces of the barometric vessel C-3301 and water seal vessel C-3302 have no corrosion damage.

- In 2013 during repair all heat exchangers of vacuum block were subjected special tests to determine their suitability for further use, at same time were observed deviations or loss of strength due to corrosion effects.

- At the next stage of the monitoring data were analyzed measurements of wall thickness of pipelines in vacuum unit. It was found that in some parts of pipelines according to measurements 2013 there is a reduction in metal thickness by an amount of 0.5 mm or more compared with the data of 2012 years.

Table 5 shows the point of pipelines with a reduction in the wall thickness of 0.5 mm or more with type area (bend, insert, or straight section of pipe). At the same time was taken into account only the data that well correlate with the thickness of the pipeline obtained in prior periods.

Table 5. The measurement points on the pipelines of the vacuum block with reduced thickness (s) of the walls 0.5 mm or more

Pipeline №	№ point in scheme	s2012, mm	s 2013, mm	Reduces s for 1 year, mm	Type of line
7034	3б	3,6	3,1	0,5	Insert
	3в	3,6	3,1	0,5	
	13в	3,6	3,1	0,5	
7035	18а	4,9	4	0,9	Bend
	18б	4,5	4	0,5	
	18в	4,9	4,1	0,8	
	18г	4,7	4,2	0,5	
	12в	5	4,4	0,6	
	12ж	5,1	4,4	0,7	
7036	2а	4,3	3,8	0,5	Bend
	2б	4,4	3,8	0,6	
	2г	4,7	3,9	0,8	
	3а	5	4,4	0,6	Straight
	4г	5,1	4	1,1	Bend
	10а	5,1	4,6	0,5	Straight
	11г	4,8	4,3	0,5	Bend
7037	24а	10,5	7,8	**2,7**	Straight
	24б	10,6	7,6	**3**	
	24в	9,8	8	**1,8**	
	26а	9,5	9	0,5	
7038	1а	7,4	6,8	0,6	Bend
	5б	8,4	7,8	0,6	Insert
	5в	8,6	7,9	0,7	Straight
	7в	9,9	9,1	0,8	Bend
	14а	11,8	10,9	0,9	Insert
	19в	11,7	10,9	0,8	Straight
	19г	11,9	11,1	0,8	
	20б	9,6	9	0,6	
7039	5а	5,2	4,7	0,5	Insert
	5б	5,2	4,4	0,9	
	5в	5	4,3	0,7	
7040	6г	7,8	7,3	0,5	Bend
	37г	8,1	7,5	0,6	Insert
7041	8б	10,4	9,2	1,2	Straight
	8в	9,9	9,4	0,6	
	17а	10,1	9,5	0,6	Bend
	16е	8,3	7,8	0,5	
7042	Decreasing thikbess no more than s 0.5 mm				
7043	12а	5,6	4,9	0,7	Straight
	17ж	6	5,5	0,5	Bend
	19г	7,8	7,1	0,7	
	19ж	4	3,5	0,5	
	32а	4,4	3,9	0,5	
	34а	5,5	4,9	0,6	
	34б	5,4	4,8	0,6	

The analysis of Table 5 shows that:

- All considered pipelines of vacuum unit with the exception of one have regions with a loss of metal thickness greater than 0.5 mm for the period of 1 year;

- Maximum number of sites with the loss of metal thickness greater than 0.5 mm centered on the 1 and 2 condensation stage of pipelines, from the stage 3 to 4 observed decreasing of their number.

- The greatest loss of metal thickness for 1 year fixed at point 24 a,b,c of the pipeline number 07037 with uncondensed hydrocarbon vapors from the X-3202 A/B to a vacuum ejectors of second stage, which was 2.7 mm , 3.0 mm, 1.8 mm, respectively;

- A significant number of "problem" areas, as expected, focused on the pipeline bend.

- Thickness measurement data contradict with some earlier measurement results of physico-chemical parameters (pH, Concentration of dissolved Fe ions) of condensation water and with the corrosion rate. This discrepancy is probably due to the fact that the corrosive properties of the medium ("sour" water) are unstable and may vary significantly at various in time intervals. To the aggressiveness of the environment can influence many factors: the properties of raw materials, adopted by the primary processing, loading of visbreaking feedstock, efficient adding of NaOH into feedstock in primary oil refining units, the parameters of the vacuum column, etc.

Conclusions

Corrosion monitoring of vacuum block of visbreaking unit JSC "Gazprom neftekhimSalavat" showed that in given medium the corrosion rate is 0.15-0.2 mm/year, according to the results of laboratory measurements, while at the same time, according to metal thickness measurements of piping sections the corrosion rate is 0.5-3.0 mm/year.

Corrosive effect primarily exposed on equipment made of non-resistant steel grades (pipelines, condensation-cooling equipment).

In order comprehensive and for longtime solution of the problems of corrosion and protection of all the equipment in the vacuum block we recommended developing and implementation of chemical technological corrosion protection with using reagents on the line from the column K-3301, including ejectors.

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