Wastewater cleanup method reducing corrosion impact on pipelines and equipment of oil stabilization production

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Abstract. The object of research in this article is the wastewater of oil stabilization production. Wastewater from oil refining and petrochemicals is highly toxic and poses a serious environmental hazard with existing wastewater volumes. The purification of these effluents to the parameters stipulated by the current regulatory requirements is practically impossible by traditional methods. In addition, in some cases, high contamination of water used in technological processes leads to significant economic losses, often irreversible. The low efficiency of wastewater treatment in the oil stabilization production negatively affects the reservoir pressure maintenance system for a number of reasons, one of which is an increased content of suspended solids that cause the formation to be calcified in the bottom-hole zone and lower well injectivity, which, in turn, leads to significant production losses oil. The actual service life of sewage pipelines containing hydrogen sulfide and oxygen does not exceed two years. The overhaul period of operation of pumps in the wastewater transport system is 0.2–0.3 years. The low efficiency of wastewater treatment is associated with the use of a morally obsolete system of treatment facilities, one of the significant drawbacks of which is the presence of open settling ponds. Lack of recycled water supply affects the costs associated with the use of fresh water. The volume of fresh water purchased for technological needs is estimated at thousands of cubic meters per day. At the enterprise under consideration, treatment facilities with a traditional technological scheme function. The authors of the article identified the reasons for the lack of effectiveness of these facilities and concluded that it is necessary to improve technologies and wastewater treatment schemes.

1. Introduction

Wastewater from oil refining and petrochemicals is highly toxic and, with the existing volumes of water disposal, poses a serious environmental hazard. Cleanup of such sewage to the parameters provided by the current regulatory requirements is practically impossible using traditional methods. Additionally, in some cases, the high pollution of water used in technological processes results in significant economic losses, which are often irreversible.
Low efficiency of wastewater cleanup at oil stabilization production negatively affects the system of formation pressure maintenance for a number of reasons, one of which is the increased content of suspended solids causing calcification of the bottomhole formation zone and reduction of injectivity of wells, which, in its turn, leads to significant losses during oil production. Actual operation life of water pipelines for transportation of wastewater containing hydrogen sulphide and oxygen does not exceed two years. The interrepair period of operation of pumps in the wastewater transportation system is 0.2–0.3 years.

Low efficiency of wastewater cleanup is connected with the use of obsolete system of cleanup facilities, one of the significant drawbacks of which is the presence of open sedimentation ponds. Sedimentation ponds do not only fail to fulfill their functional purpose, but are also the main source of associated petroleum gas pollution and oil pollution in the industrial zone, which due to incomplete extraction in the process plants are released into the open pond.

The lack of recycling water supply affects the costs associated with the use of fresh water. The volume of fresh water purchased for technological needs is estimated in thousands of cubic meters per day.

2. Purpose of the study
The purpose of these studies was to determine the chemical, hydrobiological and microbiological composition of wastewater and to develop recommendations for the reconstruction of the wastewater cleanup and disposal system.

3. Material and research methods
The wastewater cleanup installation is a part of the oil stabilization production (OSP) located in the territory of Neftegorsk industrial complex, which is a part of OGP Bogatovskneft of Samaraneftegaz JSC.

The existing sewerage and wastewater cleanup system was put into operation more than 30 years ago. By the present time, its facilities and equipment have become obsolete and have significant physical wear and tear.

The installation includes the following facilities.
- Pumping station (SPS-2), designed to supply industrial wastewater for cleanup into the ponds of additional sludge of the pumping station (SPS-3).
- Control chambers in front of SPS-2, designed for collection of industrial sewage coming through the system of gravity-flowing sewerage from the technological installations of Oil gathering station and Gas Processing Plant.
- Ponds of additional sedimentation (left and right) 2 pcs. with capacity of 5 thousand m³ each, designed for collection and primary sedimentation of formation and industrial wastewaters.
- Ponds of additional sedimentation (left and right) 2 pcs. with capacity of 10 thousand m³ each, designed for the second stage of mechanical cleanup of all sewage from oil and mechanical impurities.
- Regulating tanks in front of SPS-3, 2 pcs. with capacity of 1,000 m³ each and designed to collect cleaned wastewater from the ponds, as well as to receive excess oil-field water from the preliminary water discharge unit, which is not accepted at the BPPS-1.
- Pumping station SPS-3, which provides the supply of a mixture of cleaned formation and industrial wastewater to the water flooding systems at BPPS-1 and BPPS-2.
- Sludge storage pits are intended for storing oil sludge discharged from the ponds of additional sedimentation.
- Pumping station (SPS-4) is designed to supply trap oil from the ponds of additional sedimentation to the tanks of crude oil.
- Receiving chambers in front of SPS-4 are 2 pieces, each with a capacity of 10 m³, used to receive and collect trap oil from the ponds of additional sedimentation.
Productivity of the wastewater cleanup installation is 12,000–14,000 m$^3$/day, including Industrial – 6,000 m$^3$/day, which are subject to cleanup of formation water from crude oil reservoirs and preliminary water discharge unit – 6,000–8,000 m$^3$/day.

Pumping station SPS-3 capacity, feeding a mixture of formation water from Preliminary water discharge unit and cleaned-up waste water 16,000–19,000 m$^3$/day, including cleaned-up waste waters (a mixture of formation and industrial waste waters) 12,000–14,000 m$^3$/day; formation waters from Preliminary water discharge unit (excess not accepted at BPPS-1) – 2,000–5,000 m$^3$/day.

Raw materials for the wastewater cleanup installation of the Neftegorsk industrial complex include:

- formation wastewater from the preliminary water discharge unit, crude oil tanks, desalting and oil stabilization units (units 1 and 2);
- industrial wastewaters from the Neftegorsk GPP, oil treatment shop of OGPDU "Yuzhorenburgneft", wastewaters after regeneration of the boiler room filters, wastewaters of oil pumping stations and gasoline storage, wastewaters after flushing filter presses for sludge processing installation;
- trap oil from sedimentation ponds and sludge processing installation;
- bottom sediment of sedimentation ponds.

Commodity products of the installation are:

- formation waters treated from oil and mechanical impurities and prepared for injection into productive layers of the oilfields;
- excess formation waters treated from oil and mechanical impurities and subject to disposal in the absorbing horizons of OGPDU "Bogatovskneft" fields;
- industrial wastewaters that are cleaned-up together with formation waters from oil and mechanical impurities with subsequent joint disposal;
- relatively clean waste waters of the oil gathering facility and the gas processing plant discharged into the Siezzhaya River and partially used without treatment for flushing filter presses of the Andrits oil sludge processing installation;
- domestic wastewater treated in the filtration fields and discharged into the Siezzhaya River;
- collected oil from sedimentation ponds and from the oil sludge processing installation, which is returned to raw material reservoirs;
- the cake – the solid phase of the sludge after it has been processed.

The total amount of formation waters discharged from Preliminary water discharge unit averages 19,000 m$^3$/day. The main amount of formation water is supplied without additional cleanup to the system of formation-pressure maintenance at BPPS-1, and the excess of 2,000–5,000 m$^3$/day, which is not accepted by BPPS-1, goes to SPS-3 and further either to the water flooding system or to the absorption system.

The waterflooding system from SPS-3 receives formation water in a mixture with production wastewater, and the excess of these waters, which is up to 7000 m$^3$/day (on the injectivity of wells) is sent to the system of absorption of OGPDU "Bogatovskneft" oilfield.

The composition of the industrial wastewater discharged by gravity to the cleanup constructions is subject to significant fluctuations both in consumption and in the quality of the pollutants.

The approximate amount of these waters is 6,000 m$^3$/day.

Relatively clean wastewater comes from GPP and oil gathering facility and from blowing boilers of the boiler room in the amount of up to 4,500 m$^3$/day.

Domestic wastewater is treated independently in the filtration fields and discharged into the Siezzhaya River.

Trap oil from sedimentation ponds is characterized by water cut from 30 to 43 %, oil density is 0.890 g/cm. The amount of oil captured is approximately 150 m$^3$/hour.

The bottom oil sludge obtained from the cleaning of sedimentation ponds is stored in sludge collectors.
Table 1. Results of chemical analysis of wastewater samples of Neftegorsk industrial complex of OGPD "Bogatovskneft"

| Parameter  | Vertical stock tank-11 | Vertical stock tank-12 | Vertical stock tank-10 | SP | TS-2 Preliminary | S-2-2* water discharge unit | TS-2** | BP | U | P | O | U | P-1P-2P-3 |
|------------|------------------------|------------------------|------------------------|----|------------------|-----------------------------|---------|----|----|----|----|----|------------|
| IP         | 5.118                  | 16.764                 | 3.878                  | 1.824 | 3.268           | 3.0 2.9 28.5 6.2 498.678   | 92 3    | 89 | 55 | 7  | 62 | 94 |
| pH         | 7                      | 5.98                   | 6.93                   | 6.9 6.36.44 | 8 5 | 7.2 6.6 7.6 5.7 6.9 6.6 |
| COD        | 8000                   | 16,000                 | 76,000                 | 44,000 | 56 20 | 52 4006 0 5,2 | 000 000 | 5  | 5  | 18 |
| Total iron | 31.1                   | 17.2                   | 3.9                    | 3.5 4 3.3   | 3.7 4.1 5. 0.6 5.6 4.4 |
| Chlorides  | 225,000                | 139,000                | 13,500                 | 14,50 124,000 | 00 0 | 131 145 30 110 450350200 | 0 0 0 |
| Sulphates  | 189                    | 176.9                  | 213                    | 82.12 148 | 2 3 | 238 139 90 29. 39 43. 45 |
| Nitrogen ammonia | 62.1          | 80.6                   | 10.6 58.217           | 95 4 | 74 81.3 44. 10.4 17 |
| Nitrate nitrogen | n/d                 | n/d                    | n/d                    | n/d n/d | n/d | n/d n/d | n/d n/d |
| Nitrate nitrogen | n/d                 | n/d                    | n/d                    | n/d n/d | n/d | n/d n/d | n/d n/d |
| Petroleum products | 1.39            | 0.73                   | 4.04                   | 0.4 3.96.93 | 8.5 | 7.8 | 9. 30. 0.6 1.4 88 |
| Phosphates  | 0.69                   | 0.39                   | 0.4 0.70.35           | 7 8 | 0.6 0.4 0. 0.7 0.3 0.4 0.5 |
| Sulfides    | 50.4                   | 51                     | 51.8                   | 47.47 47.4 | 7 9 | 47. 50 | 51 296 44. 50. 47 |

TS-2* – Electric dehydrator
TS-2** – Electric dehydrator settling tank

Analysis of the samples taken from the process units and lines of oil gathering facility of the Neftegorsk industrial complex (Table 1, Table 2) shows that the following waters are formed, which differ in the composition of pollution, namely, contaminated with:

- oil;
- chloride salts;
- demulsifiers;
- iron sulphides;
- suspended solids;
- used reagent solutions.

According to the degree and nature of pollution, in order to find an optimal solution to the problem of wastewater disposal, the oil gathering facility can be divided into two groups:

The first group of wastewater combines wastewater with a high degree of contamination and, after mechanical cleanup, is designed to be pumped into the absorbing horizons and to maintain formation pressure.

The second group of waste water combines relatively clean water, which together with domestic wastewater can be cleaned-up at the biological cleanup facility and used for technological needs of the oil gathering facility, for example, for salt washing in TS-1 and TS-2.
Table 2. Results of hydrobiological and bacteriological analysis of wastewaters of neftegorskoye industrial complex of OGPD "Bogatovskneft"

| Parameters | Vertical stock tank 11 | Vertical stock tank 12 | Vertical stock tank 10 | SPS-2 | Electric dehydrator | Preliminary water discharge unit water supply to formation pressure | Settling pit, TS-1 | Access to the BPPS feed to the formation-pressure maintenance | UON | Notes |
|------------|------------------------|------------------------|------------------------|-------|---------------------|-----------------------------|---------------------|-----------------------------------------------|------|-------|
| Colour     | transparent            | dark                   | light-grey             | yellow| light-grey          | grey                        | cream               | whitey                                         | yellow|         |
| Smell      | kerosene               | oil                    | kerosene and H₂S oil  | kerosene H₂S | oil                | H₂S                        | oil                 | H₂S                                           |       | - no film |
| Presence of oil film | -                      | -                      | +                      | +      | -                   | -                           | -                   | -                                             | -     | + film  |
| Presence of sediment | black                | no sediment            | slight                 | black, pieces of petroleum products | plant   | black, dirt, pieces | different inclusions | no sediment | brown                                      |       |         |
| Opalescence | -                      | -                      | opalescence            | -      | -                   | opalescence                 | -                   | +Small single-celled flagellates               |       |         |
| The presence of protista | -                    | -                      | -                      | +      | -                   | -                           | -                   | +                                             |       | + detected |
| Bacteriological analysis | 1. CRP              | +                      | +                      | +      | -                   | -                           | -                   | -                                             | -     | not detected |
| Thion bacteria | +                    | +                      | +                      | +      | +                   | +                           | +                   | +                                             | +     |         |

The main amount of formation water discharged from the Preliminary water discharge unit is supplied without additional cleanup to the system of formation-pressure maintenance at BPPS-1.

Table 3. Results of spectral analysis of sludge from cleanup facilities of Neftegorskoye industrial complex of OGPD "Bogatovskneft".

| Cu  | Zn  | Pb  | Ni  | Co  | Cr  | V   | Ti  | Mo  | Sn  | Y   | Be  | Ga  | Ba  | Zr  | Sr  | Mn  | Sc  | Cd  | Li  | Yb  |
|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| 8   | 8   | 2   | 3   | 0.6 | 4   | 2   | 100 | 0.15| 0.15| 0.8 | 0.1 | 0.5 | 80  | 6   | 200 | 80  | 0.4 | 1   | 1   | 0.1 |
| 4.7 | 8.3 | 1.6 | 8   | 4   | 8.3 | 15  | 570 | 0.11| 8   | 2.8 | 0.6 | 1.5 | 65  | 20  | 340 | 100 | 0.6 | 0.008| 6.5 | 0.033|

Note: the table shows the data on the content of elements, 10 - 3 % of masses.

The average content of elements in the Earth's crust is highlighted in italics.

The research was carried out in production conditions at the Bogatovskneft oil gathering facility of the Neftegorsk industrial complex located in Samara Region. The staging of the cleanup process at the existing cleanup facilities was shown. Mechanical wastewater cleanup units are presented on the basic scheme of bottom-up and wastewater discharge at OGPD oil gathering facility "Bogatovskneft" (Figure 1).
The research was carried out within 2 months in connection with the identified task. Wastewater samples were taken from various oil gathering facility cleanup installations, immediately delivered to the laboratory and tested. The chemical composition of the samples studied is presented in Table 1.

Hydrobiological analysis of the same wastewaters was carried out on site with the help of the Biolam microscope at the magnification of 7x40 on the slide. The data obtained indicate the absence of the protista in the samples, which suggests the toxicity of these wastewaters (Table 2).

In the Bacteriological Analysis (Table 2), hydrocarbon oxidizing bacteria (Oxidizing bacteria (OBBs) were primarily taken into account, and their release was carried out on Raymond’s selective medium. According to the results of preliminary identification, the microorganisms were attributed to species: Pseudomonas, Rhodococcus u Arthrobacter in the amount up to $10^5$-$10^6$kl/ml.
Figure 2. Recommended scheme of existing bottom-up and wastewater discharge at oil gathering facility OGPD "Bogatovskneft".

The analysis of oil sludge cake from sedimentation ponds can be highly informative. Cake samples after annealing were examined by spectroscopic method. The results of the spectral analysis are given in Table 3. On the basis of this analysis data, the release of cadmium, the content of which in the studied samples exceeded the average concentration in the Earth's crust by more than 100 times, can be promising at oil sludge utilization. In general, the content of the detected elements does not pose a risk in cake use, e.g. in road construction as a base.

The results of chemical tests have shown that the higher the content of petroleum products in the samples up to known limits, the longer their oxidation time in natural conditions.

It becomes obvious that the movement of anthropogenic load as a result of more intensive development and operation of the oilfield can lead to a total accumulation of oil products in the water, leading to the formation of zones of anthropogenic pollution of wastewater by oil products, which will require, along with natural mechanisms of self-purification, additional conditions.
4. Findings and conclusions

By the results of the carried out tests it is possible to identify the basic directions on the intensification of resource saving technological processes and elimination of negative manifestations during pipelines and the equipment operation in the aggressive hydrogen sulfide environment.

1. In order to save fresh water used in technological processes, it is necessary to provide for cleanup of water coming from the gas plant, Yuzhno-Orenburgneft, Steam/water supply shop and domestic sewerage in the amount of up to 900 m$^3$/day at the microbiological cleanup installation. The purified water is reused in the technological process.

2. To use a system of sealed drainage, including vertical dynamic settling pits (excluding horizontal static sedimentation ponds):
   - preventing pollution of the industrial zone with associated gas and oil,
   - slowing down the process of biocorrosion in the conduit system as a result of reduced microbiological contamination of wastewater,
   - eliminating the formation of colloidal particles as a result of chemical reactions when mixing wastewaters of different chemical compositions and penetration of suspended solids into the formation pressure maintenance system.

3. For more complete degassing of formation water it is necessary to use the method of ejection discharge. To provide for the installation of ejectors on the III stage of separation bullets for more detailed degassing. The degassing of formation water will significantly reduce the concentration of iron sulphide and improve the dynamics of suspended solids deposition from wastewater in vertical settling pits. In addition, a decrease in hydrogen sulfide concentration in the formation water will lead to a decrease in bacterial contamination of the wastewaters and, consequently, to a slowdown in microbiological corrosion processes.

4. To reduce the processes of corrosion destruction of technological equipment, it is necessary to apply corrosion inhibitors Recod-602, Aminkor concentrate (TS 2415-006'1115987 3-96) and I-21-D (TS 38.403229-89).

5. Fiberglass pipes are used to transport corrosive media, such as oil-water emulsion and water entering the formation pressure maintenance system, where possible.

6. To carry out the researches on studying microbiological corrosion processes in water conduits of the formation pressure maintenance system and methods of pipeline protection from microbiological corrosion with the use of equipment for studying the condition of the inner surface of the pipeline, including methods of radiation treatment of the inner surface of pipelines.

7. The release of cadmium, the content of which in the tested samples exceeded the average concentration in the Earth's crust by more than 100 times, can be very promising at oil sludge utilization. In general, the level of content of the detected elements does not pose a risk in cake use, e.g. in road construction.

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