Process Water Production for Oil and Gas Utility Systems at High Water Color Index Conditions

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Abstract. The article is devoted to the water treatment of high water color index waters for oil and gas utility systems at low temperatures conditions. The relevance of the article is justified by the development of pipeline transport in the regions of Eastern Siberia and the Far East. The purpose of the article is to provide an empirical presentation of the feasibility and efficiency of reactant treatment of high water color index waters at low temperatures by the example of real waters of the Lena River (Eastern Siberia) and the Zeya River (Far East).

1. Introduction

Currently, the requirements for the quality of industrial water are not unique but are established by the conditions of its use in relation to specific production or household purposes. In industrial water depending on the direction of its use, the content of some impurities, for example, suspended solids, hardness salts, pH and others, can be regulated.

The paper discusses energy carriers of Irkutsk region and Yakutia that supply consumers in Far East as well as countries of the Asia-Pacific region (primarily China), The development of the oil and gas industry towards Eastern Siberia and Far East turns the problem as the problem of first-rate importance.

The rivers of Eastern Siberia and the Far East are potential sources of water for oil and gas facilities and could be characterized as low-mineralized, with low turbidity but with a high chromaticity and a negative Langelier stability index. The low temperature, which is observed for most of the year in these regions, complicates the treatment of water, including reagent water.

Process water should not only be low-mineralized, have little suspended solids (suspended solids content no more than 5 mg / l, salt content no more than 500 mg / l, pH (7 - 8), nitrates (2 - 4) mg / l, nitrites (0.03 - 0.06) mg / l, chlorides and sulfates not more than 120 mg / l), but it should also have a low color. [1]

* In the numerator - in the presence of copper-containing alloys in the steam-water mixture, in the denominator - in the absence of them;
** In the numerator - for CTPP (condensing thermal power plants) and heating CHP plants, in the denominator - for CHP plants with production steam extraction.

One of the problems of water supply is the purification of high-color low-turbidity river waters. Turbidity of water is determined by the content of particles of mineral origin (silt, sand, clay, etc.). Color is the degree of color of natural waters, expressed in degrees of platinum-cobalt scale, due to the
content of humic and fulvic acids. Humic and fulvic compounds do not precipitate even after long standing.

These compounds form the basis of the organic part of natural waters. The amount of these substances depends on many factors. The main ones are:
- geological conditions;
- characteristics of the mechanical composition of soil;
- aquifer;
- the presence of peat bogs;
- stagnant waters in the river basin.

Common ways to reduce color are:
- oxidation (with chlorine or chemical elements suitable for these purposes);
- the use of substances that cause flocculation followed by mechanical filtration;
- adsorption by active carbons;
- filtration.

To increase the efficiency of color reduction, water is treated with chemical reagents - coagulants (most often salts of trivalent metals) and flocculants. Since many reagents do not work well in cold water, the goal was to experimentally select coagulants and flocculants for the treatment of waters of Eastern Siberia and the Far East, which can work at low temperatures of the treated water, because the average annual temperature does not exceed (5 - 7)°C.

For example, Lena (Eastern Siberia) and Zeya (Far East), experiments were carried out to reduce the color (clarification) of waters. Water samples from both rivers were taken for quality indicators. Water samples of Lena were taken during the flood period, because this period provides for high chromaticity. Water samples of Zeya have a low chromaticity, because they were taken in the period before freeze-up, but when the water has a low temperature that makes it possible to pick up reagents at a temperature of 2°C.

Sampling was carried out with entry into the river, from the middle layers of the water column at a depth of 2 m. Data for Lena and Zeya are given in table 1.

**Table 1. Qualitative indicators of the Lena and Zeya.**

| №  | Indicator                        | Indicator | Test results, sample from the Lena River from 05/17/2019 | Test results, sample 1 from the Lena River from 05/15/2019 | Test results, sample 2 from the Lena River from 05/15/2019 | Test results, water sample from the Zeya river from 10/23/2019 |
|----|---------------------------------|-----------|----------------------------------------------------------|----------------------------------------------------------|----------------------------------------------------------|----------------------------------------------------------|
| 1  | Suspended substances            | mg/dm3    | less 0,5                                                 | 6,4                                                     | 7,6                                                     | 5,2                                                     |
| 2  | Hydrocarbons                    | mg/dm3    | 79,3                                                     | 29                                                      | 31                                                      | 39,7                                                    |
| 3  | Total hardness                  | mg-eq/dm3 | 1,8                                                      | 0,79                                                    | 0,84                                                    | 0,90                                                    |
| 4  | Mineralization                  | mg/dm3    | 140,1                                                    | 178                                                     | 153                                                     | 165                                                    |
| 5  | Chromaticity                    | deg.      | 426                                                      | 470                                                     | 488                                                     | 41,0                                                    |
| 6  | Alkalinity                      | mg-eq/dm3 | 1,3                                                      | 2,6                                                     | 2,8                                                     | 0,65                                                    |
| 7  | pH Petroleum derivatives (total)| mg/dm3    | 7,24                                                     | 7,9                                                     | 7,9                                                     | 6,75                                                    |
| 8  |                                 |           | up to 0,005                                             | 0,04                                                    | 0,05                                                    | <0,05                                                   |
The experiments were carried out on water samples immediately after sampling. In the course of research on clarification of river water, it was treated with various reagents. The results were evaluated visually. The samples that showed the best result were sent for laboratory analysis. During the experiments, the water temperature regime was maintained corresponding to the water temperature in the river. To ensure the required temperature, the initial water after sampling was placed in a refrigerator.

Widely used, available, working on natural waters of a given quality (pH, temperature, etc.) were considered as coagulants. Polyoxychloride aluminum, sodium aluminate, ferric sulfate and polyDADMAC are satisfying these requirements.

2. Experiments on water clarification of the Lena river
To test the possibility of oxidation of organic compounds, including chromaticity, the river water was treated with sodium hypochlorite. Two samples were prepared with doses of 150 mg/l and 300 mg/l for the active substance.

In the first 2-3 hours after entering the chemical agent visual discoloration is not observed. Visual discoloration begins to appear after 6 hours of sedimentation and reaches a maximum value after 12 hours of sedimentation.

Due to the high dose of the chemical agent and the required significant contact time, the use of sodium hypochlorite on an industrial scale without additional research is not appropriate.

Further experiments were carried out on the selection of a coagulant. The following coagulants were taken: polyaluminum chloride, ferric sulfate and ferric chloride.

For experiments were chosen polyaluminum chloride (Figure 1) and ferric sulfate (Figure 2) at doses of active substance 30 mg/l, since this dosage and coagulants showed the best result.

|   | Chemical Element | Unit | Dose (mg/dm³) 1 | Dose (mg/dm³) 2 | Dose (mg/dm³) 3 |
|---|-----------------|------|----------------|----------------|----------------|
| 9 | Sulfate-ion     | mg/dm³ | 12.89 | 15 | 16 | 6.23 |
| 10| Chlorides      | mg/dm³ | 7.22  | 1.2 | 1.3 | 2.21 |
| 11| Silicon        | mg/dm³ | 2.19  | 3.4 | 3.4 | 3.60 |
| 12| COD (chemical oxygen demand) | mg/dm³ | 56.15 | 4.6 | 4.7 | 27.0 |
| 13| Aluminum       | mg/dm³ | 0.267 | 0.38 | 0.39 | 0.46 |
| 14| Ferrum         | mg/dm³ | 0.514 | 0.38 | 0.39 | 0.46 |
| 15| Calcium        | mg/dm³ | 24.903 | 10 | 11 | 5.90 |
| 16| Magnesium      | mg/dm³ | 7.900 | 3.4 | 3.5 | 1.2  |

Figure 1. Coagulation with polyaluminum chloride in doses of active substance 10, 20, 30 mg/l (from the left to the right).

Figure 2. Coagulation with ferric sulfate in doses of active substance 10, 20, 30 mg/l (from the left to the right).
Further experiments were carried out on the choice of a flocculant working in conjunction with the selected coagulants.

For the experiments were taken by one of each type of flocculant (non-ionique, cationic and anionic):
- Zetag4100 – non-ionique flocculant;
- Zetag8125 – cationic flocculant;
- Zetag4120 – anionic flocculant.

According to the experiments on the selection of a flocculant, the cationic Zetag 8125 at a dosage of 5 mg/l with both ferric sulfate and polyaluminum chloride fare better.

The samples were filtered and sent for analysis to the laboratory. The results of the analysis of the filtered test samples are shown in table 2.

| № | Indicator                          | Units     | Test results, ferric sulfate with addition of a flocculant | Test results, polyaluminum chloride with addition of a flocculant |
|---|-----------------------------------|-----------|------------------------------------------------------------|------------------------------------------------------------------|
| 1 | Suspended substances              | mg/dm³    | 7,0                                                        | 7,2                                                              |
| 2 | Hydrocarbonates                   | mg/dm³    | 10                                                         | 23                                                               |
| 3 | Total hardness                    | mg-eq/dm³ | 1,2                                                        | 1,4                                                              |
| 4 | Mineralization                    | mg/dm³    | 150                                                        | 136                                                              |
| 5 | Chromaticity                      | deg.      | 147                                                        | 250                                                              |
| 6 | Alkalinity                        | mg-eq/dm³ | 2,9                                                        | 3,6                                                              |
| 7 | pH                                |           | 5,8                                                        | 7,2                                                              |
| 8 | Petroleum derivatives (total)     | mg/dm³    | 0,23                                                       | 0,14                                                             |
| 9 | Sulphates                         | mg/dm³    | 14                                                         |                                                                   |
| 10| Sulfate-ion                       | mg/dm³    |                                                             | 145                                                              |
| 11| Chlorides                         | mg/dm³    | 1                                                          | 5                                                                |
| 12| Silicon                           | mg/dm³    | 0,5                                                        | 0,5                                                              |
| 13| COD (chemical oxygen demand)      | mg/dm³    | 7,8                                                        | 8,2                                                              |
| 14| Ferrum                            | mg/dm³    | 0,16                                                       | 0,05                                                             |
| 15| Calcium                           | mg/dm³    | 21                                                         | 23                                                               |
| 16| Magnesium                         | mg/dm³    | 1,8                                                        | 2,7                                                              |

As a result of filtration of the test sample with a coagulant (ferric sulfate) in a dose of 30 mg/l and a cationic flocculant Zetag 8125 in a dose of 5 mg/l, a residual was obtained. The residual contains the large flakes with a density close to the density of water, as a result the residual is light and can migrate (float) in the water column with temperature or flow convection. For sedimentation of such residual, it is recommended to use sedimentation tanks with thin-layer modules and (or) carry additional weighting agents (previously formed sediment, microsand) into the water. Filtration of the test sample (to separate it from the residual) showed that the residual offers mudding properties.

3. Experiments on water clarification of the Zeya river

10% solutions of polyaluminum chloride, sodium aluminate, ferric sulfate, 5% aluminum sulfate solution and 1% polyDADMAC solution were prepared.

To test the coagulants, a dose of 30 mg/l for the active substance was added to the river water (since, using the example of the Lena river, it was determined that lower dosages did not show the required result). The first check was carried out at a temperature of 5 °C to determine the operation of
the reagent with this water, if the reagent works, the next check was carried out at a temperature of 2 °C to determine the operation of the reagent at the low temperatures.

During the experiments, only a sample with the addition of sodium aluminate showed a positive result. A visible layer of residual appeared after 5 minutes of sedimentation. All flakes have landed after 30 minutes of sedimentation. The worst result was shown by the ferric sulfate (figure 3).

Figure 3. Test sample with the addition of sodium aluminate, initial water of the Zeya river, test sample with the addition of ferric sulfate (from the left to the right).

Figure 4. River water with 10 mg/l sodium aluminate and 20 mg/l aluminum sulfate (left) and river water with 10 mg/l sodium aluminate and 20 mg/l polyaluminum chloride (right).

In order to test the operation of coagulants in the mixture and reduce the consumption of expensive sodium aluminate, it was decided to conduct an experiment on river water at the temperature 2 °C with a mixture of coagulants 1/3 sodium aluminate and 2/3 polyaluminum chloride, and 1/3 sodium aluminate and 2/3 aluminum sulfate. All further experiments were carried out with water at the temperature not higher than 2 °C.

River water with the addition of a mixture of sodium aluminate and aluminum sulfate showed a much worse result than with the addition of 10 mg/l sodium aluminate and 20 mg/l polyaluminum chloride (figure 4).

According to the results of all experiments, the best result was obtained by treating water with a mixture of sodium aluminate coagulants and polyaluminum chloride.

Further experiments were carried out on the selection of a flocculant working with the selected coagulants. The flocculant should provide effective clarification at lower doses of coagulant and promote a higher degree of clarification.

During experiments with flocculants, the dose of coagulants was twice as little (5 mg/l sodium aluminate and 10 mg/l polyaluminum chloride).

For the experiments were taken by one of each type of flocculant (non-ionique, cationic and anionic) similar to experiments with the water of the Lena river.

According to the results of the experiments, the best were a mixture of coagulants 10 mg/l sodium aluminate and 20 mg/l polyaluminum chloride and a mixture of coagulants 5 mg/l sodium aluminate and 10 mg/l polyaluminum chloride with cationic flocculant Zetag8125 1 mg/l. The samples were filtered and sent for analysis to the laboratory. The results of the analysis of the filtered test samples are shown in table 3.
Table 3. Results of laboratory analysis of clarified samples from the Zeya river.

| №  | Indicator                        | Units       | Test sample 1 (10 mg/l sodium aluminate and 20 mg/l polyaluminum chloride) | Test sample 2 (5 mg/l sodium aluminate and 10 mg/l polyaluminum chloride with addition of cationic flocculant 1 mg/l) |
|----|----------------------------------|-------------|---------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------|
| 1  | Hydrocarbonates                  | mg/dm3      | 62,2                                                                      | 42,7                                                                                                    |
| 2  | Total hardness                   | mg-eq/dm3   | 1,21                                                                      | 0,67                                                                                                   |
| 3  | Dry residue (total dissolved solids) | mg/dm3      | 102                                                                      | 88,0                                                                                                   |
| 4  | Chromaticity                     | deg.        | 7,70                                                                      | <5                                                                                                       |
| 5  | Alkalinity                       | mg-eq/dm3   | 1,02                                                                      | 0,70                                                                                                   |
| 6  | pH                               |             | 7,31                                                                      | 6,83                                                                                                   |
| 7  | Sulphates                        | mg/dm3      | 10,4                                                                      | 4,60                                                                                                   |
| 8  | Chlorides                        | mg/dm3      | 11,3                                                                      | 18,1                                                                                                   |
| 9  | Silicon                          | mg/dm3      | 2,40                                                                      | 1,40                                                                                                   |
| 10 | Aluminium                        | mg/dm3      | 0,10                                                                      | 0,065                                                                                                  |
| 11 | Ferrum                           | mg/dm3      | 0,041                                                                     | <0,01                                                                                                  |
| 12 | Calcium                          | mg/dm3      | 7,90                                                                      | 11,0                                                                                                   |
| 13 | Magnesium                        | mg/dm3      | 1,30                                                                      | 2,1                                                                                                     |

According to the results of experiments were determined reagents providing chromaticity reduction of river water.

When using a mixture of coagulants (10 mg/l sodium aluminate and 20 mg/l polyaluminum chloride), the efficiency in reducing chromaticity was 81,22%.

When using a mixture of coagulants and flocculants (5 mg/l sodium aluminate and 10 mg/l polyaluminum chloride with a cationic flocculant 1 mg/l), the efficiency in reducing chromaticity is 87,8%.

In addition to a decrease in chromaticity, a decrease in the amount of silicon, aluminum and iron ions is observed.

As a result of filtration of test sample 1 and test sample 2 a residual was obtained.

The residual contains the large flakes with a density close to the density of water, as a result the residual is light and can migrate (float) in the water column with temperature or flow convection. Filtration of the test sample (to separate it from the residual) showed that the residual does not offers mudding properties.

Thus, based on the performed experiments, the most effective coagulants for the water of the Zeya and Lena rivers were selected. For the Zeya river the most optimal is a mixture of coagulants and a flocculant (5 mg/l sodium aluminate and 10 mg/l polyaluminum chloride with cationic flocculant Zetag 8125 1 mg/l), and for the Lena river – polyaluminum chloride 30 mg/l and cationic flocculant Zetag 8125 5 mg/l. Different rivers have different chemical compositions and it is necessary to select coagulants individually for each water by experiment. Experiments have shown that it is possible to work with reagents at low temperatures with a good end result: obtaining technical water from high-chromaticity river water.

4. References
[1] GOST17.1.1.04-80 Klassifikaciya podzemnyh vod po celyam vodopol'zovaniya
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[3] Abramov N N 1974 Vodosnabzhenie: Uchebnik dlya vuzov (M.: Strojizdat) p 480
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