Equipment and technology for wastewater post-treatment for returning it to production cycle

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Abstract. Given there is development of state-of-the-art technologies in the field of water treatment and the demanding requirements for environmental control, as well as trends in the cost increase of chemicals and usage costs of primary resources, it deemed necessary to modernize the water treatment and water purification systems in such a way as: firstly, to minimize discharges as such; secondly, to increase the degree of use of circulating water; thirdly, using modern non-reagent cleaning technologies to minimize the consumption of necessary chemical agents, which has a complex effect – both in merely economic terms (procurement, transportation, storage, movement and control), and from a practical perspective – increasing the environmental safety of production, area release, etc.

1. Introduction
The development and implementation of such (low/non-reagent, low/non-waste) water treatment and water purification technologies (and, in fact, the reconfiguration of thermal-and-hydraulic decoupling of TPPs) are currently actively used not only abroad, but also in Russia. For example, the introduction of low-waste and non-reagent technologies, as well as the creation of hydraulically tight cycles at the boiler house TPP-6 of the Omsk TPP, achieved the following performance targets over 7 years [1,2]:

- water discharge reduced from 916 to 250 thousand tons/year (from 16 to 4.9 %);
- specific water flow reduced 3.7 times – from 0.73 to 0.2 m³/Gcal;
- The discharges of pollutants from the boiler house decreased:
  - for petroleum products – from 1.33 to 0.194 tons/year;
  - by suspensions – from 10.64 to 4.05 tons/year;
  - for iron – from 183 to 35 kg/year;
  - salt intake and discharge decreased from 1616 to 286 tons/year.
2. Discussion
Based on the experience of operating various technologies and comparing the results, it was noted that the most promising technologies for treating low mineralization waters with a high content of organic impurities (surface waters of the central and northern parts of the Russian Federation) are counter-flow ionization and desalination based on membrane technologies. The high quality of chemically purified water with a large unit capacity of ion-exchange filters is ensured by deep control automation, both by individual filters and by the entire unit.

Operation experience of counter-flow technologies has shown their advantages in comparison with conventional ones: quantity reduction of necessary water treatment equipment; high exchange capacities of ion exchangers; high quality filtrate, and quantity reduction of highly saline wastewater [3-5].

However, due to the lack of a second (barrier) stage and the difficulty of determining the moment of output to regeneration, the deactivation of a counter-flow filter is often carried out according to the amount of passed water on the safe side, which leads to under-production of demineralized water. In counter-flow regeneration, the intensity of regeneration increases and, as a result, the number of switchings, which requires both highly qualified personnel and reliable specialized valves, automation and control, greatly depends on the quality of water clarification and a high degree of its purification from suspended particles, organics and iron compounds.

Therefore, the higher the quality of incoming water, the higher the efficiency of a counter-flow.

Recently, much attention has been paid to low-reagent methods, and primarily membrane technologies. Some new WTPs are based on the use of reverse osmosis for demineralization of water using mechanical filters as a pre-treatment.

The use of reverse osmosis makes it possible to extract up to 96–98 % of salts at a single purification step, which is close to the efficiency of a single ion exchange step. The permeate post-treatment system can consist of an ion exchange stage with separate H- and OH-ionization (direct-flow or counter-flow) and (or) with a mixed-bed filter (MBF).

Since partially demineralized water is supplied to such a plant, the filter resource is considerable and reaches tens and hundreds of thousands of cubic meters.

Below is the schematic diagram of water treatment using a reverse osmosis unit (operated by Ivanovskiy PGU OJSC):

![Figure 1. Diagram of a water treatment system using a ROU: FW – feed water; Cl – clarifier; CWT – clarified water tank; MF – mechanical filter; Na — Na cation exchange filter; FOA – organic absorber filter; C – coagulant; SW – slime waters; DW – demineralized water; HD – hard drain; ROU – reverse osmosis unit; MBF – mixed-bed filter.](image)

3. Results
Comparison of the economic efficiency of water desalination by ion exchange and reverse osmosis showed that with a salt content of more than 150–300 mg/L reverse osmosis is more cost efficient than even counter-flow ionization [3,4,5].
The available experience in operating reverse osmosis units (ROUs) indicates that the main factor the operation of the membranes depends on the observance of the quality standards of the water supplied to the input of the reverse osmosis unit.

For the membranes to work effectively, it is essential that the feed water meet certain requirements (see Table 1).

| Parameter                                              | Value      |
|--------------------------------------------------------|------------|
| Temperature, °C                                        | up to 45   |
| Free chlorine concentration, mg/L                      | up to 0.1  |
| pH while in operation                                  | 2–11       |
| pH while rinsing                                       | 1–12       |
| Iron concentration, mg/L                               | up to 0.1  |
| Organic matter content in total organic carbon (TOC), mg/L | up to 0.3  |
| Manganese concentration, mg/L                          | up to 0.1  |
| Turbidity, NTH                                         | up to 0.1  |
| Concentration of oils and petroleum products, mg/L     | up to 0.1  |
| Silt density index SDI                                 | up to 5    |

An analysis of these requirements shows that there are no limitations on the salt content of surface waters of natural sources. Only the content of those substances that can lead to "poisoning" or clogging of membranes is limited.

Water clarification quality parameters which are traditional for water treatment (concentration of suspended solids, cross turbidity, transparency, color, oxidizability) do not give an adequate idea of the relationship between membrane performance and contamination of their surfaces and pores with sediments of suspended and colloidal particles. Manufacturers of reverse osmosis elements evaluate the quality of treated water, first of all, by SDI indicator (silt density index, SDI). The maximum permissible value of SDI is 5, with SDI values of 3 to 5, such waters are classified as complex, and stable operation of the reverse osmosis element is guaranteed at SDI <3.

Pilot-plant operation of various combinations of purification systems shows that in schemes with traditional pre-treatment technology, the quality of water supplied to a reverse osmosis unit, as a rule, does not meet the requirements for iron content and oxidizability. The required quality of such water can be achieved by ultra-filtration at the pre-treatment stage (Figure 2).

![Figure 2](image_url)

**Figure 2.** Scheme of a combination mount for the preparation of deeply demineralized water using ion-exchange post-treatment: D – decarbonizer; GBC – get break container; SWMF – self-washing mechanical filters; BD – buffer drums; UFU – ultrafiltration unit; ROU – reverse osmosis unit; PDWT – partially demineralized water tank; H – H cation exchange filter; A – OH-anion exchange filter; AWW – acid waste water; AW – alkaline waste.
The use of ultra-filtration technologies allows one not only to obtain water that is practically free of mechanical impurities, but also, together with coagulation, to remove a significant amount of organic matter (up to 60% of the initial amount), as well as silicic acid.

As an example, below are the results of the operation of the ultra-filtration unit (UFU) at the Cherepovets SDPP (the water-supply source is the Suda River) (Table 2).

| Parameter                      | Feed water | Filtrate |
|--------------------------------|------------|----------|
| Total hardness, mEq/L          | 0.7        | 0.7      |
| Total alkalinity, mEq/L        | 0.6        | 0.012    |
| Oxidizability, mgO₂/L          | 36.8       | 9.2      |
| Chloride concentration, mg/L   | 3.3        | 16       |
| Iron content (total), mg/L     | 1.93       | 0.085    |
| Aluminum content, mg/L         | –          | 0.016    |
| Colour                         | >80        | 25       |

The introduction of ultra-filtration at the pre-treatment stage significantly increases the performance of reverse osmosis membranes, several times reduces the frequency of chemical washes, and also frees up production areas, reduces the consumption of coagulant, and allows one to completely give up on lime.

The combined use of ultra-filtration and reverse osmosis makes it possible to create a low-reagent water treatment system to obtain a filtrate with a specific conductivity of 1–5 μS/cm.

In such schemes, the water quality is usually brought to standard values by the ion-exchange method (see Fig. 2).

The reliability of such a combined ion-exchange membrane unit is quite high, since even with possible failures of a reverse osmosis system, the post-treatment unit will provide the specified water quality.

At the same time, the above scheme still requires the use of acid and alkali, therefore this technology, although to a lesser extent, has the same drawbacks as the conventional one.

The major drawback of all membrane systems is a rather low feed water utilization factor. If in the conventional ion-exchange scheme with coagulation and mechanical filtration, own needs are 10–20%, then for a typical combination of ultra-filtration and reverse osmosis, this figure is 40–50%. However, it should be borne in mind that concentrates from ultra-filtration and reverse osmosis units in terms of salt content are often within the normalized values and do not require additional purification before discharge.

Combined ion-exchange membrane schemes, which have a high degree of economic efficiency and reliability, are the most optimal and recommended method for the reconstruction of available water treatment systems that already have ion-exchange filters, chemical plants, and waste collection and neutralization systems. In this case, the amount of concentrated wastewater and the consumption of reagents is ten times less than with an ion-exchange scheme alone, and wastewater of this quality can be diluted to the permissible levels with concentrate of membrane units.

From the point of view of ensuring the minimum consumption of reagents and the most environmental friendliness with high quality demineralized water, the maximum efficiency is shown by comprehensive water treatment systems consisting exclusively of membrane modules for various purposes: ultra-filtration and nano-filtration, reverse osmosis, membrane degassing and electrodeionization, referred to as integrated membrane technologies (IMT) [6,7]
The schematic diagram of such a unit (IMT) is given below:

![Diagram](image)

**Figure 3.** Scheme of a comprehensive plant for the preparation of deeply demineralized water using post-treatment by electrodeionization: D – decarbonizer; GBC – get break container; SWMF – self-washing mechanical filters; BD – buffer drums; UFU – ultrafiltration unit; ROU – reverse osmosis unit; PDWT – partially demineralized water tank; PTEU – post-treatment-by-electrodeionization unit.

In a comprehensive membrane plant (Figure 3), water is treated at the electrodeionization unit. Electrodeionization (EDI) is a process of continuous water demineralization using ion-exchange resins, ion-selective membranes and a constant electric field.

When the degree of feed water utilization is 90–95 %, purified water has a specific conductivity of 0.1 μS/cm, as well as a minimum silica content and total organic carbon.

In this case, the salt content of a concentrate is usually lower than the salt content of water supplied to a reverse osmosis unit; therefore, it all returns to the input of this unit for reuse.

All manufacturers of electrodeionization units have very high requirements for water supplied to a unit, regardless of its design (Table 3).

To increase the reliability of comprehensive membrane water treatment systems based on integrated membrane technologies, the use of a two-stage reverse osmosis at the stage of preliminary demineralization is required.

**Table 3.** General requirements for feed water for electrodeionization plants

| Feed Water Parameters                  | Values   |
|---------------------------------------|----------|
| pH                                    | 5÷9      |
| Electrical conductivity, μS/cm        | <20      |
| Total hardness, mg/L CaCO 3           | <1.0     |
| Total organic carbon, mg/L            | <0.5     |
| Free chlorine, mg/L                   | <0.05    |
| Fe compounds, mg/L                    | <0.01    |
| Silica content (SiO 2), mg/L          | <1.0     |
| Carbon dioxide concentration (CO 2), mg/L | <5.0   |
| Turbidity, NTU                        | <1.0     |
| Operating temperature, °C             | 5–45     |
| Inlet pressure, atm.                  | 0.7–5.0  |

In this case, the quality of water feeding the electrodeionization plant is obviously higher than the requirements for reverse osmosis plants and any operation deviations become noncritical. If the efficiency of the first stage decreases (within acceptable limits), the specified water quality will fully ensure the next stage.

A comprehensive membrane plant for the preparation of deeply demineralized water, made in accordance with the above scheme (Figure 3), provides a minimum amount of waste. In addition, there is no need for acid-base plants, operating costs are reduced and the environmental characteristics of the entire system are significantly improved. Such comprehensive membrane plant has been successfully operated at Pervomaisk TPP-14.
4. Conclusion
With the overall effectiveness of the above technological solutions and the experience gained, it seems promising to apply a number of similar technologies at the Sakmarskaya TPP.

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