PROCESSING OF ALKALINE WASTEWATER OF TPP EVAPORATIVE WATER TREATMENT PLANT WITH ELECTROMEMBRANE METHODS

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Abstract. The thermal desalination technology is considered one of the most environmentally friendly and perfect for the preparation of steam turbine additional water. The purging water of the evaporative unit is an alkaline, highly mineralized, intensely colored solution, in which sodium salts (sulfates, chlorides) and alkali are mainly contained. The total salt content exceeds 30 g/kg. There is significant content of organic substances, silicates. A technology has been developed for processing of a thermo-desalting complex purge water by electromembrane methods to produce alkali and softened water. A schematic solution of the electromembrane utilization of purge water excess from an evaporator water treatment plant is presented.

Water treatment schemes using thermal desalination technology are currently used at a number of thermal power plants (TPPs), both in the Russian Federation and abroad, namely, Saransk TPP, Kazan TPP-3, Rostov TPP-2, Omsk TPP-5, Surgut state district power station, etc. The main elements of such schemes are surface type evaporators, during which operation purging water of high mineralization is formed. Analysis of thermal desalination plant operation shows that their use allows to significantly reduce the source water consumption, reduce the waste water discharge and the chemical reagent consumption which largely fits into concept of drainage and wastelessness of industrial and energy enterprises companies adopted in recent years [1, 2]. Within this concept, a set of technological solutions for rational water use was developed Kazan TPP-3 with the introduction of a low-waste water treatment plant on wastewater heat-treated additional water for boilers, as well as sludge and chemical reagents suitable for further use in the technological process [3].

Table 1. Average data on the composition of evaporative water treatment plant purging water. [4].

| Index                | Concentration       |
|----------------------|---------------------|
| pH                   | 13.2-13.7           |
| Alkalinity           | 95-100 mg-eq/dm³    |
| Total hardness       | 0.45-0.85 mg-eq/dm³ |
| Carbonate hardness   | 0.25-0.54 mg-eq/dm³ |
| Total salt content   | 10-45 g/l           |
| Na⁺                  | 19-41 g/dm³         |
| SO₄²⁻                 | 9900-20009 mg/dm³   |
| Cl⁻                  | 2150-4500 mg/dm³    |
| Cu²⁺                 | 0.25-1.15 mg/dm³    |
| SiO₂                 | 280-440 mg/dm³      |
| Fe³⁺                 | 9.8-1.7 mg/dm³      |
| Suspended substances | 96-147 mg/dm³       |
In the process of the described technology implementing, an excessive amount of purging water of the evaporative plant is formed, an average 0.8-1.0 m³/h (Table 1).

Purging water is a highly mineralized solution that contains mainly sodium salts (chlorides, sulfates) and a large number of insoluble impurities – iron, copper, silicon compounds. In addition, natural high molecular weight organic compounds are present. These impurities are mostly in the colloidal state, or go into a colloidal state during the water treatment. Hence the need is to separate small and insoluble impurities before and during processing. In the purge water there are also organic substances of natural origin. This is evidenced by the color of the water – dark brown. There is no chemical analysis for organic substances content [5].

It should be noted a large amount of alkali (4-8 g/l, depending on the month) in the evaporators purge water. This fact is of fundamental importance for a technical solution (scheme) of purge water recycling.

Water treatment schemes with significant or complete wastewater elimination of can be realized with the electromembrane device help [6]. Taking into account the given data on the purge water composition and the requirements for the resulting solutions, electromembrane treatment can be realized successively in steps on three types electric-membrane apparatus:

1) alkali separation from salts;
2) salts decomposition into alkali and acid;
3) water desalination and alkaline solution concentration.

The investigations were carried out using EMA-100 experimental-laboratory electromembrane apparatus, developed by us [7], with a maximum chamber number of 100. Using membranes were of the «Shchekinoazot» (Russia).

The purge water Scheme of the three-stage treatment of is shown in Fig. 1.

**Fig. 1. Utilization of evaporator purging using electromembrane modules for alkaline and acidic solution obtaining (shortened): I – electromembrane alkali separation; II – bipolar electromembrane apparatus; III – electromembrane concentration, desalination.**

At the first-stage, a partial alkali separation from the initial solution in the EMA with cation and anion exchange membranes occurs. The driving force of the process is the higher hydroxyl ion mobility in comparison with sulfate and chloride ions. Since the process selectivity is not high, it is possible to as produce an alkaline solution containing the initial solution salts as the product.
The EMA of the first stage produces a concentrated alkaline solution and diluat I. The latter is a more diluat solution of the starting salts and the remaining alkali. Diluat I is the starting solution for the second-stage EMA.

The EMA of the second-stage is assembled with bipolar membranes and serves to separate the solution of salt into alkaline and acidic solutions. As products in the second-stage, a diluat II is formed, which is a more diluat solution of the starting salts, unconcentrated alkali solutions and acids mixtures. Diluat II is sent to the EMA of the third-stage, the alkaline solution is concentrated on the first-stage or to the EMA alkali concentrator. An acidic solution containing a sulfuric, hydrochloric and nitric acid mixture, is sent to the consumer.

On third-stage EMA, the process of the diluat II concentration-desalination is carried out to produce partially desalted water with a salt concentration of about 0.3 g/l (diluat III) and concentrate. Diluat III is used to prepare alkaline and acidic solutions in the second stage of EMA.

The presented scheme is flexible enough. It is possible to gradually reduce the steps, starting with the last. If you remove the EMA third-stage (concentration-desalination), partially desalinated water for second-stage can be taken from the water treatment plant.

Equivalent water amount in the diluat II form (sodium salt solution) is directed to make up the heating network. That is, water is exchanged between water treatment and electromembrane plants. With the reduction of the third- and second- stages simultaneously an alkaline solution and diluat I can obtained on the electromembrane apparatus of the first-stage. Alkaline solution is sent to concentration or directly to the consumer. Diluat I (saline solution) can be used for the regeneration of Na-cation exchanger filters, for the heating system replenishing or for the evaporator replenishing.

To obtain a cleaner alkali and a more concentrated acid solution, it is necessary to install one more type of EMA concentrator (Fig. 2).
EMA, the alkali concentration in the alkaline solution will be from 4 to 8 mass. %. As impurities, the initial sodium sulfate and sodium chloride salts are present up to 10 % of the base material.

The second product – an acidic solution contains the initial salt and a mixture of sulfuric with inclusions of hydrochloric and nitric acids. Depending on the degree of salts decomposition at the second-stage of electromembrane treatment, the acids concentration can vary from 0 to 3 %. In the extreme case, when the salts are completely decomposed, approximately equal amounts of alkaline and acidic solutions are obtained.

If it is decided to limit the alkaline and saline solutions production, a second-stage electromembrane treatment of the purge water is possible (Fig. 3). The scheme includes the alkaline solution the separating and concentrating steps.

Fig. 3. Scheme of purge utilization with pure concentrated alkali and saline solution obtaining: IV – electromembrane preparation of alkali of the second-stage.

The resulting concentrated alkaline solution (concentrate) is sufficiently high purity and can be used in the plant cycle to regenerate the anion exchanger filters. The softened salt solution can be fed to the heating system.

Thus, it is economically and technically simple to obtain concentrated alkaline and soft salt solutions by electromembrane methods, with their further utilization in the station cycle.

At the same time, the acid production in its pure form is difficult. It is possible to obtain only the acids mixture (sulfuric, hydrochloric and nitric). Further separation seems economically inexpedient. This limits the scope data the acid mixture application in the plants process cycle.

**Conclusions**

1. The composition data of the evaporative water treatment plant purge water are analyzed. A large alkali amount in the evaporative plant purging water is of fundamental importance for the choice of the technical solution for purging. The electromembrane technology using represents an opportunity for purging water separation into separate components and their subsequent utilization in the technological cycle.

2. In accordance with the electromembrane processing features and limitations, the requirements for the conditions and quality of the treated water and the obtained solutions are formulated.

3. The schemes of evaporators purging water electromembrane processing have been developed, allowing to allocate valuable raw materials reusable in the production cycle:
- scheme for alkaline and acid solutions obtaining from the evaporators purging water;
- shortened scheme for alkaline and acid solutions obtaining;
- scheme for alkaline and softened solution obtaining.

4. Relatively low operating costs make the most expedient use of the scheme of purging water utilization with concentrated alkaline and softened salt solutions obtaining, which are used in the station cycle. For industrial development, the described scheme is recommended.

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