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Purification of acidic highly mineralized spent regeneration solution of Novo-Salavatskaya TPP

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Annotation. The results of laboratory studies and industrial experiments on the neutralization and purification of highly mineralized acid waste regeneration solutions of the ion-exchange water-preparation plant H-cationite filters are given. As the reagent the carbonate sludge from the pre-cleaning of the water treatment plant was used. A sludge was used in a dry dehydrated form. During a laboratory study, it was shown that there are a significant sulfate content reduction and a pH increase. The sulfate determination was carried out by turbidimetric method using a Shimadzu UV-1800 spectrophotometer. The water treatment sludge using at Novo-Salavatskaya TPP is able to reduce the sulfate content in acid waste water from 16.8 g/l to 1 g/l. This way of neutralizing can reduce these penalty sanctions for thermal power plants for wastewater discharge.

Introduction

The creation of thermal power plants (TPPs) with a minimum harmful impact on the environment (environmentally friendly TPPs) is without a doubt one of the most important scientific and technological task. With limited natural fresh water and constant deterioration of the water sources condition while the requirements stricter of regulatory authorities to the discharged sewage quality, the assessment of the TPPs environmental impact becomes one of the main criteria for the operation effectiveness.

Based on laboratory studies and industrial experiments a new method for purifying highly mineralized wastewater from sulfate-containing components is proposed, on the example of Novo-Salavatskaya CHP.

Theoretical part

The main problems of water use in thermal power plants are:

- large volume of highly mineralized wastewater (WW) from water treatment plants (WTP). On average, their volume is up to 25% of the chemically desalted water (CDW) production;
- the sulphate content in the WW WTP is highly overestimated, which caused the huge fines presence;
- high chemical reagents specific consumption including the sulfuric acid for the regeneration (110 g/geq);
- problems with wastewater treatment plants and waste storage, while increasing production of chemically desalted water (CDW). Lack of space and equipment.

A radical way to reduce water consumption and protect water bodies from pollution is the water losses reduction and the reuse of sewage in the TPP technological cycles. The experience shows that with repeated use wastewater, in most cases, a smaller depth of purification and therefore less cost than with WW discharge into water bodies are required.



- To reduce water consumption and WW discharge, the most promising directions are:
- the maximum application of recycling water management systems;
 - the re-consecutive water use in several technological cycles;
 - the water treatment method application, as a result of which WW are not formed at all or can be used in other cycles directly or after appropriate treatment;
 - the allocation and use of valuable substances contained in WW production .

“Traditional” scheme, pre-cleaning-ionite desalination, includes bleach with liming and coagulation or only with coagulation, mechanical filters (MF) with appropriate loading, one or two ion-exchange (IE) stages, figure 1. This scheme is considered “classical” for the water preparation for steam and condensate losses replenishment on power units with type boilers. Therefore, utilization of highly mineralized acid spent regeneration solutions is of great importance in the water treatment system.

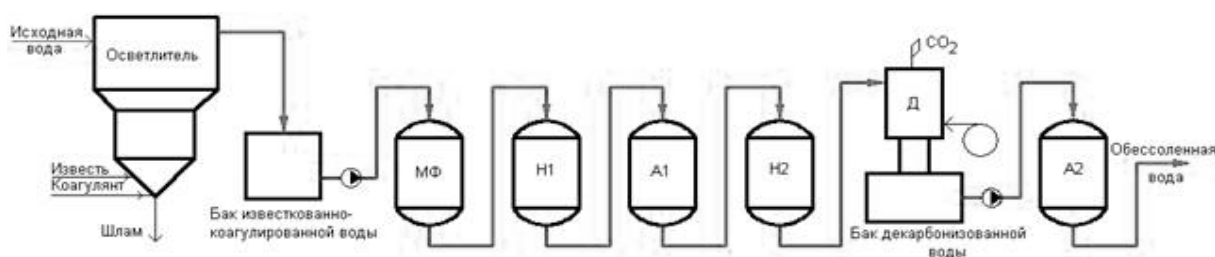


Figure 1. Water desalination classical scheme

When pre-cleaning, slurry water with a solids concentration of 5 to 50 kg/m³ is formed. Further clarified water after pre-cleaning passes the ion-exchange treatment. After the ion-exchange part chemically demineralized water is obtained. As ion-exchange filters, strongly and weakly acidic cation exchangers H⁺ and Na⁺, strongly and weakly basic anion exchangers in OH⁻ or salt form are used.

The H-cationite filters regeneration is carried out by inorganic sulfuric acid of various concentrations (from 0.8 to 4%). To ensure the necessary depth of the cation exchange regeneration, the regeneration solution consumption in most cases is 2-3 times higher than the stoichiometric amount. As a result of chemical purification, sewage is formed, which contains all the reagents excess, and also Ca²⁺ and Mg²⁺, which enter it during the regeneration process. In the process, a large number of acidic, highly mineralized wastewaters are formed. There are many difficulties in processing and disposal of these wastes, since the sulfate content is very high.

There are various methods for wastewater treatment, but each method has its drawbacks: the use of expensive reagents, the water purification insufficient, the used reagents toxicity and the inability to use on an industrial scale. Therefore, a new technology is needed that would satisfy all the requirements for wastewater treatment.

Description of the principle technological scheme of the WTP at the “Novo-Salavatskaya” TPP

The wastewater treatment plant is designed to wastewater treat from mechanical impurities and petroleum products to a content of: mechanical impurities – no more than 3 mg/dm³, petroleum products – no more than 0.3 mg/dm³ with their supply to the cooling tower or to the sewage treatment plant of “GazpromneftekhimSalavat”.

On the pre-cleaning, which is carried out by the liming coagulation method with iron salts, carbonate sludge is formed as a solid waste. Its composition is determined by the component composition of the natural water and is approximately the same for TPPs in the central Russian Federation part terms of dry matter, the sludge consists of approximately 80% calcium carbonate (CaCO₃), 15% magnesium hydroxide (Mg(OH)₂), 2% iron hydroxide, the remainder is other impurities (SiO₂, organic substances). WTP slurry is an alkaline calcium-containing reagent. Consequently, its expected action is similar to the lime.

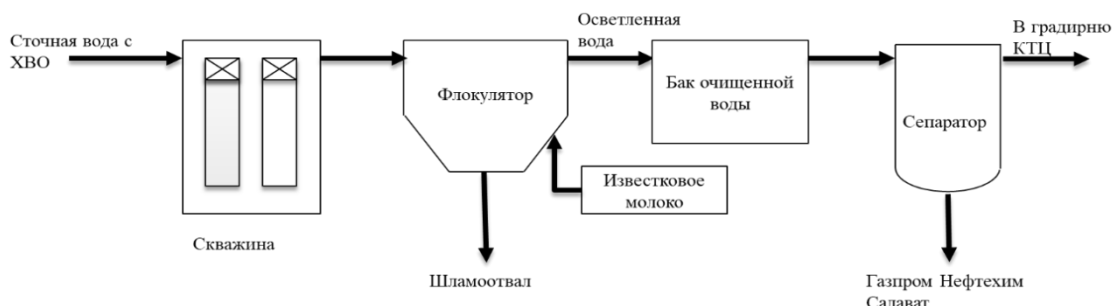


Figure 2. Schematic diagram of the wastewater treatment plant at the Novo-Salavatskaya TPP.

Laboratory research

For laboratory experiments was provided from Novo-Salavatskaya TPP. In the form of a calcium-containing reagent, the slurry waters if thermal power plants were used. The sludge content in the slurry water is about 2%

The Novo-Salavatskaya TPP provided different water kinds: slime water; water from the washing of the H-cation filter first stage; water from the washing of the Na-cation filter first stage; water from the neutralizer tank.

In the laboratory, the analysis of the provided water was carried out, during which the following water characteristics were measured: pH, conductivity, the sulphate content. Table 1 shows the results. The following equipment was used: UV spectrophotometer Shimadzu-1800, conductivity meter HannaHI 9033. The method sulfates determination was the turbodimetric method.

Table 1. Waters characteristics of the Novo-Salavatskaya TPP.

Name	Appearance	pH	Conductivity	Sulphate content
Sludge water	Color: yellow-brown. There is a dispersed phase, at the bottom of the bottle a brown precipitate is observed. The slurry content in the water is approximately 2%.	10,29	0,23	0,04
The first stage of the H-cation filter	Color: colorless, transparent. At the bottom of the bottle a white precipitate is observed	1,13	More than 20	16,8
The first stage of the Na-cation filter	Color: colorless, transparent.	8,65	More than 20	0,16
Neutralizer tank	Color: yellowish color. The suspension is observed.	6,54	4,21	4,2

Before the research beginning, spectra of the investigated waters were taken with a UV spectrophotometer.

We took 100 ml of water from the first stage of the H-cation filter, in which the sulfate content was 0.175 mol/l. To neutralize sulphates, it is necessary to take sludge in a minimum molar ratio of 1:1. If you take the sludge as CaCO₃ (100 g/mole), then for 100 ml of the prepared solution you need to take a slurry of 1.75 g / 100 ml.

Water from the first stage of the H-cation filter has a pH=1.13 units. The neutralization reaction was carried out with mixing in a glass beaker in which electrodes for measuring total salinity (TS) were placed. Sludge was added in two divided doses of 1.75 g of slurry per 100 ml of water.

Figure 3 shows kinetic curves for the neutralization process.

After the reaction passing a white and brown precipitates could be observed in the beaker. /the solution os then filtered through a paper filter. The filter was under room conditions.

The filtrate characteristics pH=5.93, TS=5.87 g/kg. CaCl2 (0.175 g/mol) or 1 g was added to remove the sulphate from the neutral filtrate 1.

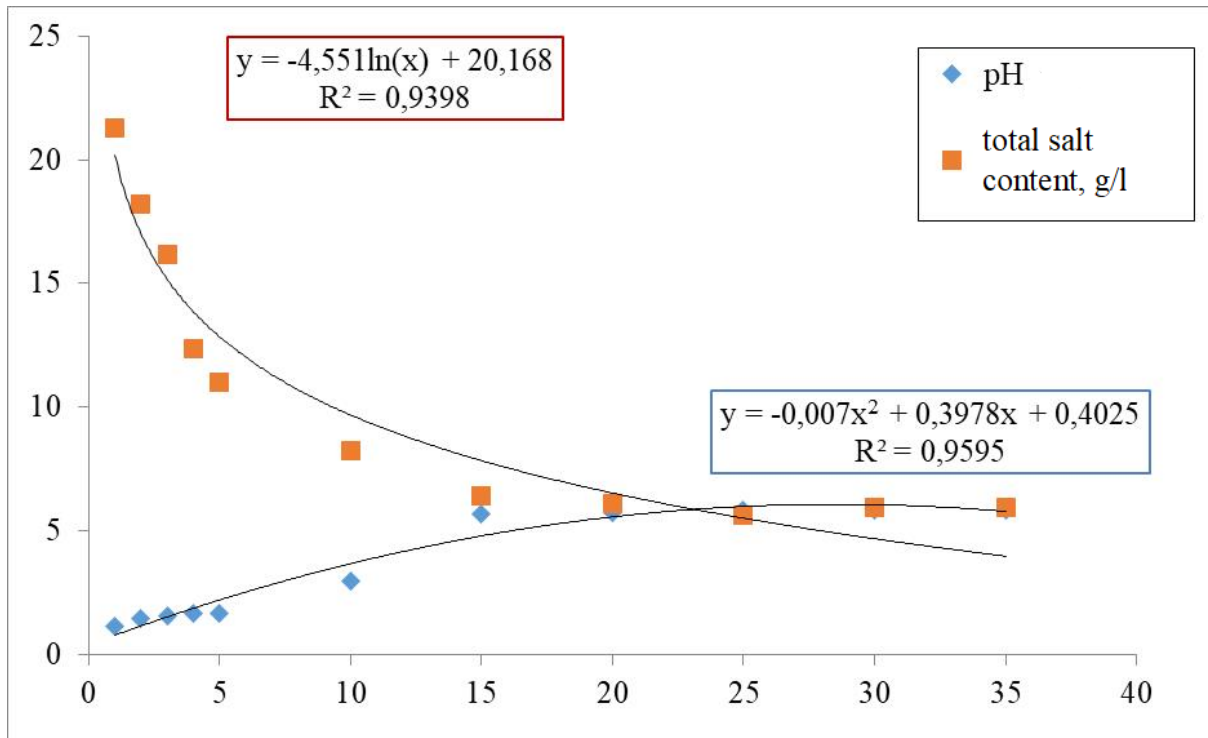


Figure 3. The change in the hydrogen index and total salt content during neutralization of the water from the first stage of the H-cation filter by pre-cleaning sludge .

The reaction kinetics are given in Table 2.

Table 2. The reaction kinetics for treating water from the first stage of the H-cation filter Further, the calcium chloride was added to the filtrage-1.

τ , min	1	2	3	4	5	10	15	20	25	30	35
pH	1,15	1,46	1,58	1,65	1,67	3,0	5,67	5,75	5,85	5,85	5,87
total salt content, g/l	21,3	18,2	16,18	12,34	11,00	8,23	6,43	6,12	5,62	5,96	5,93

The reaction kinetics are given in Table 3 and Figure 4.

Table 3. The filtrare-1 treatment reaction kinetics.

τ , min	1	2	3	4	5	6
pH	5,97	5,99	6,0	6,01	6,02	6,02
total salt content, g/l	More than 20					

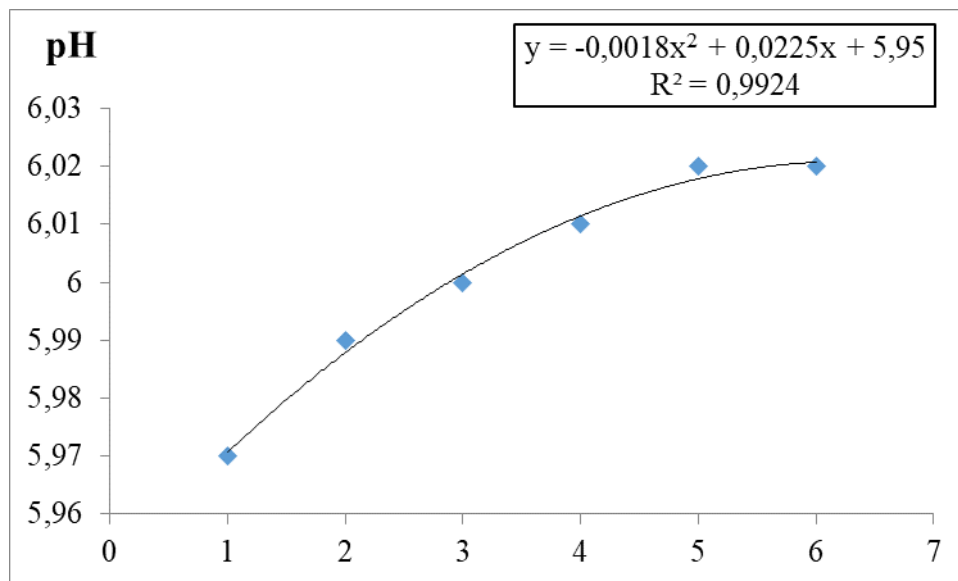


Figure 4. Change in the hydrogen index of the filtrate-1

The filtrate 1 was left for a day in a glass. During this time, a white precipitate was formed. Then the solution was filtered (filtrate-2) and the residual amount of sulfates. Has determined thus, the final results of the experiment are summarized in Table 4.

Table 4. The experiment results

Water	Sulfate content, g/l
first stage of the H-cation filter	16,8
filtrate -1	6,14
filtrate -2	0,98

References

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