STUDY OF THE POSSIBILITIES OF INTEGRATED TREATMENT OF FLUE GASES AND WASTE-WATER FROM COAL-FIRED HEAT POWER PLANTS

by

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The results of laboratory studies carried out to identify the possibility and effectiveness of technologies for the complex recycling of components of flue gases and wastewater from thermal power plants and industrial boilers are presented. The following factors were investigated: the degree of saturation of water solutions with CO_2*, the efficiency of using these solutions for the regeneration of cation exchangers, the properties of regeneration solutions intended for the regeneration of cation exchange filters prepared using components of flue gases obtained from the combustion of organic fuel in the laboratory by saturating water of various compositions, the degree of saturation of condensate and waste-water with components of flue gases, as well as the degree of regeneration of cation exchangers with such regeneration solutions. After research in the laboratory, a laboratory installation was created in an industrial environment to determine the properties of solutions obtained from wastewater and flue gases obtained after production processes at a power plant. The technologies were developed for the complex recycling of flue gases and waste-water from thermal power plants with the production of* CO_2 *with a purity of 99.9%, technical nitrogen with a purity of 95%, special solutions for the regeneration of cation exchangers in water purification plants of industrial enterprises. The results obtained make it possible to minimize the volume of emissions into the atmosphere and the volume of waste-water from thermal power plants*

Key words*: flue gases, waste-water, waste recycling, thermal power plants, water treatment, cation exchanger, regeneration*

Introduction

The studies mentioned in the article relate to engineering and technical sciences: energy, chemical technologies, environmental protection, and engineering ecology.

Harmful substances resulting from combustion in thermal power plants cause enormous environmental damage [1]. These are substances such as GHG (CO_2, water vapors H_2O), which cause a *greenhouse* effect for our planet, SO_x and NO_x, which cause *acid rain*, harmful for both humans and animals and plants [2, 3].

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Also, as a result of technological processes, acid and alkaline wastewater with high salt content is created at water treatment installations, discharge into the aquatic environment of which cause irreparable damage to the Earth's aquatic ecosystem [4].

However, the problem of environmental pollution can be solved by recycling both flue gases and wastewater, and at the same time their complete treatment will be carried out.

The aim of research is to study the composition and properties of aqueous solutions obtained by saturation of waste-water with flue gas components, as well as the possibility and efficiency of their use for their own needs of the power plant.

The results of the study contain the data on the effectiveness of the interaction between wastewater and flue gases of thermal power plants. It has been shown that gaseous sulfur oxides are efficiently interact by alkaline wastewater. But the issues of studying the possibility of gypsum formation during the cleaning of flue gases with wastewater remained unresolved [5]. The reason for this is the temporary difficulties in conducting industrial tests of these studies in winter period during the heating season. Further research will be carried out in industrial conditions in the summer on existing equipment.

Many scientists around the world are working to solve the problem of neutralization of emissions of harmful and toxic flue gases into the environment and wastewater [4]: through the liquid catalytic oxidation [6], using adsorbents prepared by high ratio circulating fly ash and lime [7], and with citric acid [8] but all of them are aimed at their treatment, rather than recycling with use at the power plant itself.

Thus, there are *dry* [9-12] and *wet* [13-15] methods for desulfurizing flue gases to obtain sulfur in various forms and compositions, as well as methods for purifying NO_x. However, the cost of each such setting is determined at the level of 30% of the cost of the products entire power plant, which increases the specific cost of the received electric and thermal energy by 15-20% [16]. Technologies existing today make it possible to purify flue gases from SO_x [17, 18] with a high degree of efficiency (about 99%). Two-stages of SO_2 absorption combined the sodium-alkali and Wellman-Lord methods. The products could be recycled as valuable pure SO_2, H_2SO_4, or Na_2SO_3. The method is limited in temperature to a value of 60 °C, which is often not sufficient for the conditions of thermal power plants. The method is more suitable for the metallurgy industry.

Technology of wastewater disposal is even less involved than flue gas disposal. Waste-water is treated from pollutants [19] that are not disposed of, but sent to special sludge sites or ash dumps, which still pollute the environment and require constant financial investments in land reclamation.

The most studies investigate flue gas and wastewater treatment separately independently of each other. The only one is exception [20], where the noted stages are carried out sequentially with the using of a bacterial consortium, as well as chemical reagents [21]. In this case, only desulfurization waste-water is treated. In contrast to all noted references, the present article authors propose to combine the stage of purification of flue gases from SO_2 with waste-water treatment. As a result, the combination leads to a significant environmental effect and obvious economic benefits due to the use of wastes as reagents.

The aim of the study is the possibility and efficiency of using regeneration solutions created or received based on waste-water and flue gases for the regeneration of cationites of water treatment plants at thermal power plants.

To achieve this aim, it is necessary to solve the following tasks:

- Conducting a study of regeneration properties of solutions prepared using flue gas components (CO_2 and acid-forming oxides) based on condensate, regeneration solutions and waste-water.

- Conducting an investigation of efficiency of using aqueous solutions saturated with flue gas components for cationite regeneration.

Materials and methods

Theory

The sum of calcium and magnesium ions (stiffness) is one of the most important indicators of water quality, determining the possibility of its use [22-24].

With a decrease in pH, the solubility of $CaCO_3$ (as a weak acid salt) increases with the formation of $Ca(HCO_3)_2$. When the pH decreases CO_3^{2-} ions as anions of weak acid react with hydrogen ions:

$$H^+ + CO_3^{2-} = HCO_3^- \tag{1}$$

In this case, the concentration of CO_3^{2-} ions decreases, the product of concentrations of Ca^{2+} and CO_3^{2-} ions becomes less than the solubility of $CaCO_3$ and some additional amount of $CaCO_3$ goes into solution.

With sulfate ions, calcium ions form a hardly soluble calcium sulfate, characterized by a sharply expressed negative solubility coefficient.

Magnesium ions as ions of a relatively weak base undergo hydrolysis, eq. (2), leading to the formation of basic ions, eq. (3):

$$H_2O = H^+ + OH^- \tag{2}$$

$$Mg^{2+} + OH^- = Mg(OH)^+ \tag{3}$$

At temperatures of about 100 °C, hydrolysis can lead to the formation of $Mg(OH)_2$.

The flue gases generated by coal combustion, contains a large content of CO_2 – from 15.2-17 %, so it was reasonable to check its effect on the regeneration process of cationite.

It is known that connection hardness salts with sulfates form gypsum, $CaSO_4$. The concentration must be strictly limited so that deposits do not form in the equipment of the gas purification circuit, which cannot be removed by using chemical reagents.

Calcium sulfate, $CaSO_4$, is an inorganic compound, which is called the calcium salt of sulfuric acid. This compound dissolves very slowly in water, hydrating to a crystalline hydrate with 1/2 or 2 molecules of water per 1 molecule of sulfate, respectively $CaSO_4 \cdot 0,5H_2O$ and $CaSO_4 \cdot 2H_2O$. Solubility decreases with increasing temperature: if it is 0.2036 g/100 g of water at 20 ° C, then it decreases to 0.067 g of sulfate per 100 g of water near the boiling point of water (100 °C). Calcium sulfate dissolved in natural water is one of the factors that determine the hardness of water. When the temperature rises, but not more than up to 180 °C, calcium sulfate dihydrate loses part of the water, turning into semi-aqueous – the so-called *burnt gypsum*, suitable for further use as a binder. Gypsum completely loses water upon further heating to 220 °C, forming anhydrous $CaSO_4$, which absorbs moisture only during long-term storage and turns into a hemihydrate.

The solubility increase of gypsum, SM_{CaSO4}, decreases with increasing of water temperature:

$$SM_{CaSO_4} = \left[Ca^{2+}\right]\left[SO_4^{2-}\right] \tag{4}$$

Also, the activity of the forming ions (cation and anion) affects the formation on efficiency (speed) process and the solubility of salts.

It is important to note that chlorine anions and hydroxyl OH^- enter into reductive reactions with cations faster than sulfates SO_4^{2-}.

On the other hand, the amount of the formed $CaSO_4$ salts consists of the formed calcium salts with chlorides and $Ca(OH)_2$, and as the second stage the remainder of calcium cations, which form gypsum with sulphate residues.

It is known that $CaCl_2$ and K_2SO_4 are formed primarily when sulfur oxides removed from flue gases come into contact with waste-water, and after that only $CaSO_4$ as a gypsum is formed in water from residual gaseous SO_2 and Ca.

The adsorption of SO_2 by water can be represented by the equilibrium expression:

$$SO_{2\text{smoke}} + H_2O \Leftrightarrow SO_{2\text{wet}} + H_2O \Leftrightarrow H^+ + HSO_3^- \Leftrightarrow 2H^+ + SO_3^{2-} \tag{5}$$

The final pH value of the solution after absorption determines in which of the forms $SO_{2\,\text{wet}}$-HSO_3^--SO_3^{2-} – the absorbed SO_2 will be.

The following equations describe the absorption of SO_2 by hard waters with high salinity and hardness:

$$CaCl_2 + SO_2 + H_2O \Leftrightarrow CaO_3 + 2HCl \tag{6}$$

$$CaSO_3 + SO_2 + H_2 \Leftrightarrow Ca(HSO_3)_2 \tag{7}$$

$$MgCl_2 + SO_2 + H_2O \Leftrightarrow MgSO_3 + 2HCl \tag{8}$$

$$MgSO_3 + SO_2 + H_2O \Leftrightarrow Mg(HSO_3)_2 \tag{9}$$

The formation of soluble bisulfites of calcium and magnesium occurs at an atomic ratio of Ca: Mg = 1:2 and a pH range of 2-4, which makes it possible to realize the process of sulfur absorption in the liquid phase and to avoid the formation of hardly soluble deposits on the surfaces of ash collection devices. An increase in the degree of gas purification from SO_2 occurs with an increase in pH, due to the fact that there is a at the same time joint absorption of carbon dioxide, starting with pH = 5:

$$CO_2 + H_2O \Leftrightarrow HCO_3^- + H^+ \tag{10}$$

The release of $CaSO_3$ and $MgSO_3$ into the solid phase occurs upon alkalinization of water that has absorbed SO_2:

$$Ca(HCO_3)_2 \xrightarrow{+OH^- + Ca^{2+}} CaSO_3 \downarrow + H_2O \tag{11}$$

In addition, the following reactions take place when using alkaline blowdown water:

$$Ca(HCO_3)_2 + SO_2 \rightarrow Ca(HSO_3)_2 + H_2O \tag{12}$$

$$2NaOH + SO_2 \rightarrow Na_2SO_4 + H_2O \tag{13}$$

Any alkaline water enhances the capture of sulfurous constituents in the gas, and can be used in wet ash collection equipment. The efficiency of desulfurization depends on the alkalinity (pH value of the irrigation water) and the salt composition.

Equipment

The preparation of CO_2 solutions in water was carried out under laboratory conditions with the help of compressed gas, the flow of which was sent to a container with a volume of 50 L, made of stainless steel, filled with distilled water. The water in the vessel was stirred with a propeller stirrer, fig. 1. The pressure in the tank was controlled by changing the flow rate of gas coming from the cylinder according to the readings of the pressure gauge. The value of the solution pH was controlled using electrodes built into the capacity and a pH-meter of the pH-150 type.

Studies of CO_2 and flue gas solutions regenerating capacity were carried out in a 15 mm diameter chromatographic column specially made of glass ion exchange filter model of a 50 mm diameter, a filter made of stainless steel with a diameter of 200 mm in the industrial boiler house of Aksu in Pavlodar region of Kazakhstan on an industrial ion exchange filter. Sulfogol was used as cationite. Its total exchange capacity is 550-600 gE/m^3, operating capacity is 300 gE/m^3. The pressure in the vessel varied from 0.1-0.5 MPaG. The solubility of CO_2 with an increase in pressure from 0.1-0.5 MPaG increased more than twice, the minimum value of pH varies from 3.7-3.48.

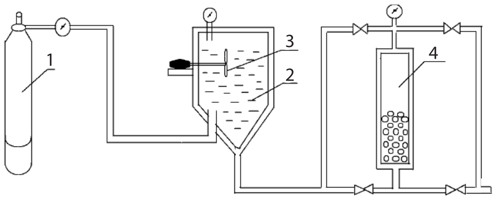

Figure 1. Diagram of the device for regeneration of cationites with flue gases or CO_2 in laboratory conditions: *1 – gas cylinder, 2 – gas solution preparation tank, 3 – stirrer, and 4 – ion exchange filter with cationite*

In a number of experiments, the regenerative ability of CO_2 solutions prepared on softened water with a sodium salt content of 2 mg-eq/dm^3 and a total salt content of 120-140 mg/dm^3 was tested. The regeneration of the filter material was carried out in the loosening mode. At the same time, at the discharge behind the Na-cation exchange filter, the pressure was maintained from 0.1-0.35 MPaG, pH 7-7.4, at a pH value of the original regeneration solution from 5.25-6.0. The total time spent on the regeneration is from 14-122 minutes and depends on the rate of passage of the regeneration solution, which was maintained, respectively, from 3-0.47 m per hour. The experiments were carried out at a temperature of the regeneration solution of 19-21°C and the volume of the solution passed per 1 m^3 of loading from 6-8.5 m^3/m^3. During the filtration cycle, the rate of water movement was maintained from 1.73-3 m per hour. The pH of the water behind the filter at the beginning of the filtration cycle was from 6.25-6.75, the filtration cycle ended at its value from 7.3-7.9 and the hardness at discharge from 1.43-1.54 mg-eq/dm^3. The water hardness at the filter inlet during operation did not exceed 1.91 with an average hardness of 1.88 mg-eq/dm^3. The results of the work performed showed that the amount of water passed through the filter cycle is from 76.7-105.0 m^3/m^3 of the loaded material. Thus, the low efficiency of the regeneration process of the cation exchanger with CO_2 in the preparation of regeneration solutions on Na-cationized water leads to the rare using of CO_2 in emergency situations only in the absence of the possibility of using more effective regeneration solutions.

In laboratory conditions, the regenerative capacity of solutions prepared using acid–forming components of flue gases from boilers burning sulfurous fuel oil was tested. Solutions for a laboratory set-up were prepared in a container by-passing through flue gas condensate. Figure 2 shows a laboratory installation on which studies of the regeneration capacity of solutions prepared using flue gases were carried out.

Low sulfur fuel oil was burned in furnace two (sulfur content is 0.36% per raw weight). The resulting flue gases were supplied by the fan – 1 through the cooler three to the saturation tank by the flue gases six under water. The gas-flow rate was measured by rotameter four. The solution was saturated with gases to the desired pH measured by pH meter – 5. The regeneration capability was tested in a filter seven filled with spent sulfugel. After regeneration, the solution was collected in tank eight.

Before the experiments, flue gas analysis was carried out under various operating modes of the equipment. Flue gases from the sampling point of the plant were fed through a rotameter to a one liter flask filled with 20% dibasic potassium phosphate solution. Before the gas was released into the atmosphere, a control flask with dibasic potassium phosphate solution

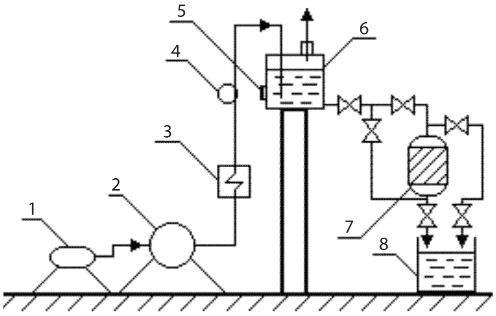

Figure 2. Diagram of a laboratory installation for the regeneration of a cation exchanger using flue gas components: *1 – fan, 2 – furnace, 3 – cooler, 4 – rotameter, 5 – pH-meter of the pH-50 type, 6 – tank for preparation of regeneration solution, 7 – cation exchange filter, and 8 – tank for collecting spent regeneration solution*

was installed. The passage of gas through the solution was carried out for 1 hour. The solution was then analyzed for HSO_3^- ion content by titration with an iodine solution, for SO_4^{2-} ions by $BaCl_2$ precipitation, for CO_3^{2-} ions by HCl titration, for NO_2 ions by $KMnO_4$ titration according to known methods. After determining the gas content in the solution, a percentage of the components in the gases was recalculated. As a result of analyses of samples, it was determined that exhaust flue gases contains sulfur dioxide SO_2^- from 0.2-0.3%, anion sulfite SO_3^- – from 0.02-0.03 %, and CO_2 – from 15.2-17%. Regeneration was performed under dynamic conditions. Dependencies of hardness dH and pH in solution samples at discharge were determined on volume of solution passed through regenerated cationite for different pH of initial regeneration solution, different volumes of sulfogal, at different temperatures and different rates of regeneration solution passage.

In the experiment it was found that if the pH value of the initial regeneration solution is 1.15, the maximum concentration of hardness ions is 30 mg-eq/dm^3, and the degree of regeneration at a ratio of the volume of the solution the volume of sulfur charcoal equal to 10 is 50%. (All regeneration characteristics were determined at a temperature of 20 °C and a linear flow rate of 4.0 m/h through a layer of cation exchanger, except where otherwise specified). Hardness and pH were determined for the entire sample taken.

The concentration of sodium chloride and sulfuric acid in the flue gas solution is 0.034 g-eq/dm^3. The degree of regeneration using the sodium chloride solution is 39%, using flue gases – 43%, the ratio of the volume of the regeneration solution the volume of sulfur charcoal in both cases is 20.

This is proof that the regeneration capacity of flue gas solutions is determined by the concentration of sulfuric and sulfuric acids therein. Sulfur anions are more active than the chlorine anion, in addition, during the ion exchange, Cl^- holds one Na^+ cation, two Cl^- anions are needed to capture the Ca^{2+} or Mg^{2+} cation. The sulfur anion contains two Na^+ cations, and one sulfur anion captures one Ca^{2+} or Mg^{2+} cation, that is, to bind the same amount of stiffness cations, the concentration of sulfur anions needs to be twice as much as chlorine anions.

A study was carried out to compare the regeneration capacity of a solution prepared using flue gas components depending on the direction of its movement: direct flow and countercurrent flow with different pass rates of 3 and 5 m per hour.

Comparative analysis showed that the degree of regeneration is greater with countercurrent movement, since ion exchange is layer-by-layer and, with softening of water with top-down movement, the upper layer of cationite works out as much as possible (a large number of stiffness ions sits there), the middle layer is partially worked, and the lower layer – practically did not participate in ion exchange. If the regeneration is carried out directly, then the calcium and magnesium ions will be taken by solution and set on cationite bonds in the lower layer. Therefore, with direct flow, the flow rate of the regeneration solution will increase. In countercurrent, the solution, passing through the lower layer, does not reduce its properties and, entering into ion exchange, takes away the hardness ions and leaves the filter.

Under laboratory conditions, regeneration with a 2% solution of sodium chloride acidified with flue gases to a value of pH = 1.8 was investigated. Experiments showed a degree of regeneration of 80-90%.

The dependence of the regenerating capacity of the sugared solution on the rate of its passage through the sulfogol during regeneration was investigated. If rate of regeneration solution passage increases from 4 to 20-25 m per hour, degree of regeneration decreases by 20% to 22%. With a similar increase in the rate of passage of the regeneration solution, the 6% sodium chloride solution is reduced by 30% to 33%. When regenerating sulfur charcoal with a solution with pH 1.8 prepared by-passing flue gases through condensate, the change in the flow rate of the regeneration solution from 4-25 m per hour slightly affects the regeneration depth and amounted to 52 at a flow rate of 2 m per hour, and 47% at a flow rate of 25 m per hour.

The regeneration capacity of the flue gas solution was checked depending on the temperature. Studies were conducted at temperatures of 20 °C, 40 °C, and 60 °C.

An inspection of regeneration ability with a temperature of solution over 60 °C was not carried out since the recommended operation temperature of the sulfur charcoal is up to 60 °C.

After laboratory studies, the question arose about the conformity of laboratory study results on the ratio of the volume of flue gases supplied to receive the necessary pH of the solution the volume of water, and the results obtained by saturation of flue gases in real conditions of fuel combustion in an industrial plant.

For this purpose, a laboratory installation was created under industrial conditions, presented in fig. 3.

The flue gases taken from the sampling point in the gas duct – 1 after the smoke exhauster two were fed under water through the rotameter three to the regeneration solution preparation tank four until the pH measured by the pH meter – 5 was saturated.

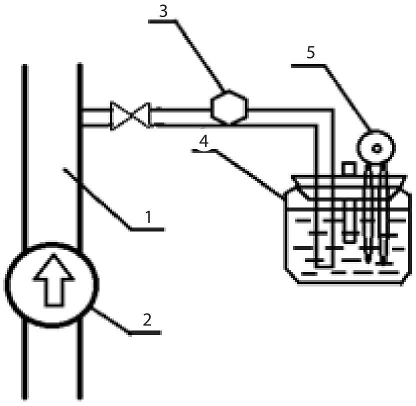

Figure 3. Research facility for preparation of regeneration solutions using flue gases in industrial conditions: *1 – gas duct between the smoke pump and the chimney, 2 – smoke exhauster, 3 – rotameter, 4 – regeneration solution preparation tank, and 5 – pH-meter of pH-150 type*

Results

The results of the study are shown below in figs. 1, 3, 5-15 and in tab. 1.

The anions with which they form the hardly soluble electrolytes, the electrolyte formulae, and the values of their solubility products (SP) are shown in tab. 1.

Figure 4 shows the change in $CaCO_3$ solubility with temperature change. The change in the solubility of CO_2 depending on pressure is shown in fig. 5.

The results of experiments on the regeneration of cationite with a solution using flue gases with an initial value pH 1.15 and a volume of cationite of 50 cm^3 are shown in figs. 6 and 7.

Figure 8 shows the dependencies of hardness and pH of solutions on the volume of solution passed through cationite for regeneration for aqueous solutions of sodium chloride and flue gases in comparison.

Table 1. Poorly soluble electrolytes, formed by calcium and magnesium ions and their SP

Anions forming poorly soluble electrolytes	Ca^{2+} ions		Mg^{2+} ions	
	Formula of the formed electrolyte	SP for 25 °C	Formula of the formed electrolyte	SP for 25 °C
OH–	$Ca(OH)_2$	$3.1 \cdot 10^{-5}$	$Mg(OH)_2$	$5.5 \cdot 10^{-12}$
SO_4^{2-}	$CaSO_4$	$6.5 \cdot 10^{-4}$	$MgSO_4$	Highly soluble
CO_3^{2-}	$CaCO_3$	$2.9 \cdot 10^{-9}$	$MgCO_3$	$1.0 \cdot 10^{-5}$
SiO_3^{2-}	$CaSiO_3$	$6.6 \cdot 10^{-7}$	$MgSiO_3$	–

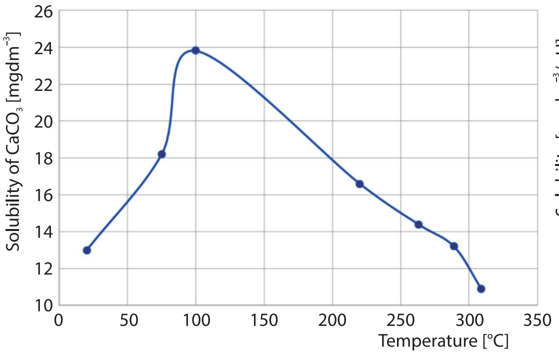

Figure 4. Temperature dependence of $CaCO_3$ solubility in water

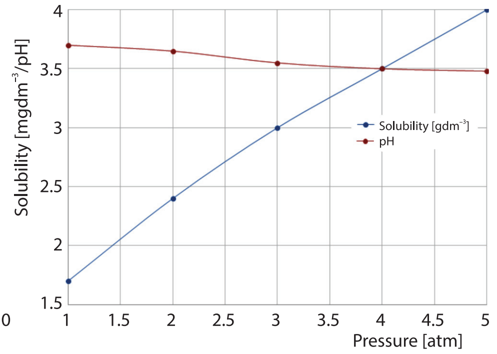

Figure 5. The CO_2 solubility and solution pH dependence on CO_2 pressure

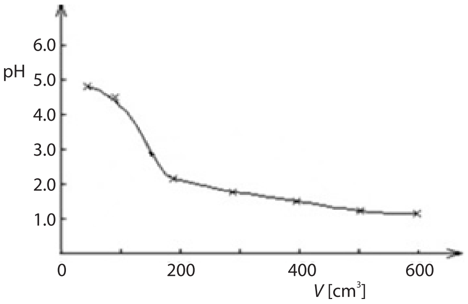

Figure 6. Dependence of pH of regeneration solution on volume of passed solution

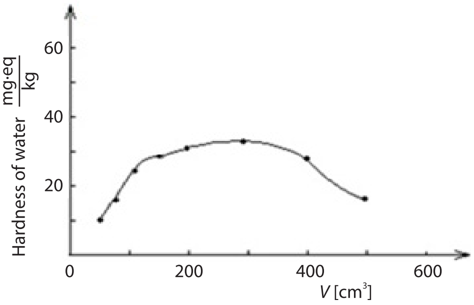

Figure 7. Dependence of total hardness of regeneration solution on volume of passed solution

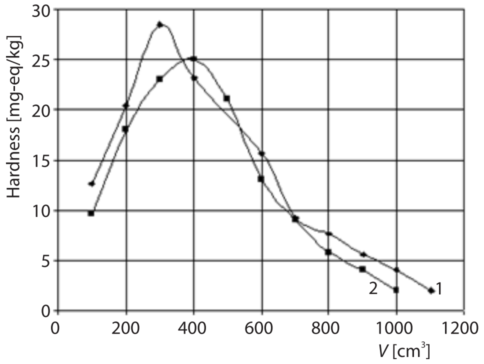

Figure 8. Comparison of regenerative capacity of aqueous solutions of sodium chloride and flue gases: *1 – salt solution and 2 – flue gas solution on condensate*

Figures 9 and 10 show the relationship between the stiffness and the pH of the regeneration solution behind the filter under direct flow and countercurrent regeneration conditions. A comparison of the dependencies for the two cases shows that the pattern of variation in stiffness in the different samples of the solution is the same and the maximum stiffness is close in magnitude. The degree of regeneration in both cases is 48-50%. The pH = *f*(*V*) curves have a greater slope to the abscissa axis for countercurrent flow.

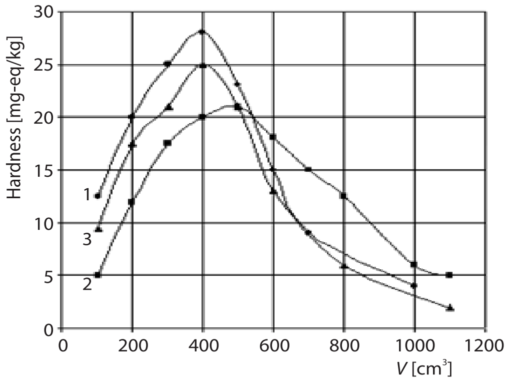

Figure 9. Dependence of hardness on the volume of the passed solution obtained using flue gases for the regeneration of sulfur charcoal at a pH of 1.8: *1 – counter flow (3 m/h), 2 – direct flow, and 3 – counter flow (5 m/h)*

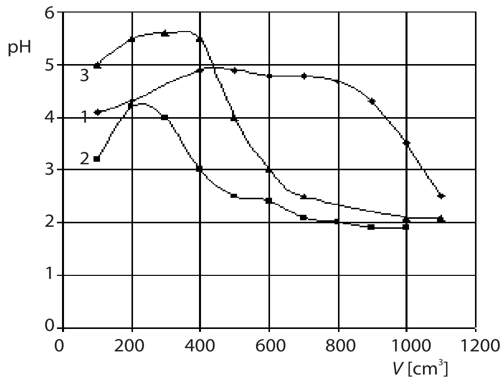

Figure 10. Dependence of pH = *f*(*V*) for counter current regeneration – 1 and countercurrent – 2, 3

Figures 11-16 show the dependencies of the stiffness and pH of the medium on the volume and velocity of the various regeneration solutions passed during regeneration in the speed range of 1.7-25 m^3 per hour. The height of the sulfur charcoal layer was in all cases the same and was 10 cm. The temperature of the regeneration solutions was 20 °C.

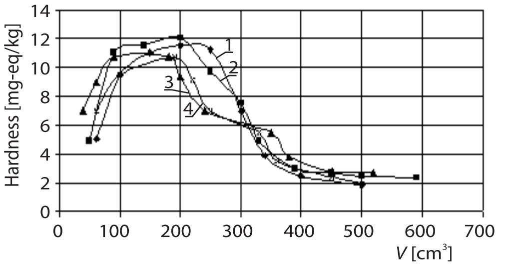

Figure 11. The dependence of the regeneration capacity of solutions prepared using flue gases on its transmission speed: *1 – 1.7 m per hour, 2 – 4 m per hour, 3 – 8 m per hour, and 4 – 25 m per hour*

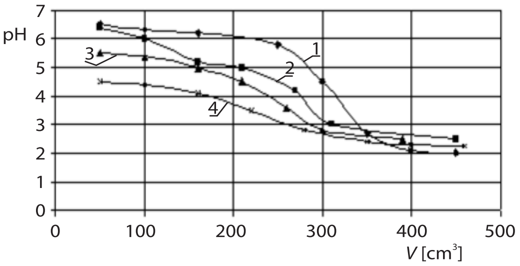

Figure 12. The dependence of the regeneration solution pH on the volume of the passed solution at various values of the pass rate: *1 – 1.7 m per hour; 2 – 4 m per hour, 3 – 8 m per hour, and 4 – 25 m per hour*

Figure 17. shows the dependence of the regeneration capacity of a solution prepared using flue gases on temperature.

Investigations were carried out for n = 3-5 parallel determinations, in addition, each experiment was carried out for m = 10-15 series. Standard deviations and probability intervals for a probability level of P = 0.95 were calculated for these experimental data samples and for each point.

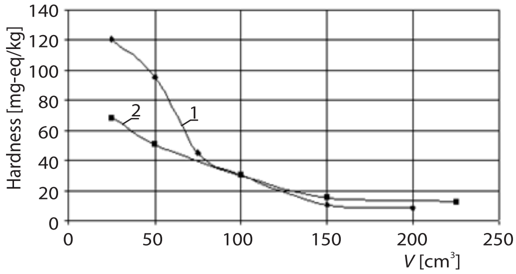

Figure 13. Dependence of pH = *f*(*V*) discharge water for NaCl solution (6%) at different regeneration rates: *1 – 4 m per hour nad 2 – 25 m per hour*

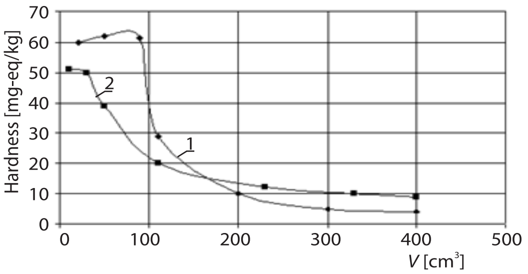

Figure 14. Dependence of pH = *f*(*V*) discharge waters for regeneration by NaCl solution (2%) at various speeds: *1 – 4 m per hour and 2 – 25 m per hour*

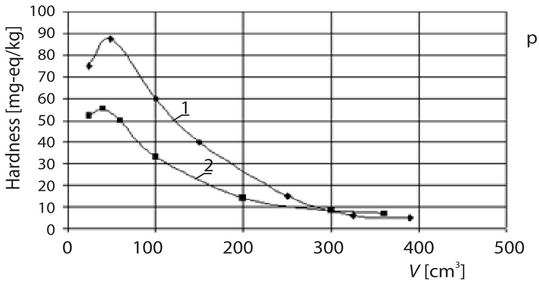

Figure 15. Dependence of pH = *f*(*V*) of discharge waters for regeneration by NaCl solution (2%) acidified by furnace gases to the pH = 1.8 at various speeds: *1 – 4 m per hour and 2 – 25 m per hour*

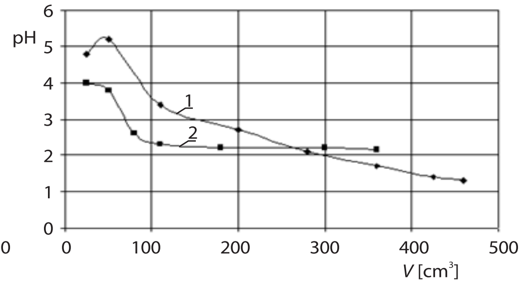

Figure 16. The dependence of the pH discharge water for the regeneration solution containing 2% sodium chloride and flue gases (pH = 1.8) on the volume of the passed solution at speeds: *1 – 4 m per hour and 2 – 25 m per hour*

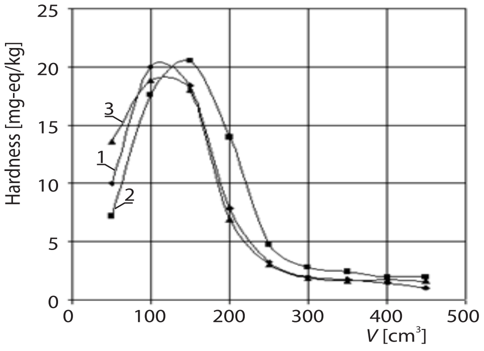

Figure 17. Dependence of regeneration capacity of solutions using flue gases on temperature: *1 – 20 °C, 2 – 40 °C, and 3 – 60 °C*

Discussion of results

When CO_2 solutions are used, the regeneration capacity of the solution is increased by lowering the pH value of the solution. However, the degree of regeneration is small: from 1-5%, with the ratio of the volume of the solution the volume of sulfur charcoal K_v up to 100. This shows that the regeneration capacity is determined by the concentration of hydrogen ions in the solution with a slight buffer effect, expressed in an increase in the degree of dissociation of carbonic acid during regeneration.

As can be seen from fig. 5, the concentration of hardness ions in the post-regeneration solution is small, and the maximum of them corresponds to the concentration of hydrogen ions in the regeneration solution of 0.001 g$^-$ion/dm^3 or the solution pH of 3. The degree of regeneration is about 1%.

For solutions of the furnace gases prepared on condensate, change of linear speeds of regeneration from 4-25 m per hour does not affect considerably dependence hardness and meaning pH from the missed. The degree of regeneration for all velocities is approximately 50%. This indicates the possibility of regeneration of cationite at speeds up to 20-25 m per hour, that is, 5-6 times greater than those used for regeneration with a salt solution and 2-2.5 times greater than for regeneration with a sulfuric acid solution.

When checking the effect of temperature on the regeneration capacity of flue gas solutions, the degree of regeneration increased with increasing temperature and reached 41%, 42%, and 47%, respectively, that is, the increase in temperature slightly affects the degree of regeneration.

Studies on a laboratory installation showed a coincidence in the volume ratios of flue gases passing through water to reach a certain pH both in the first and in the second research facility in the power plant.

During the studies, it turned out that with the repeated use of waste-water, saturating it several times with flue gases, the time of the filter cycle and the efficiency of the regeneration solution increases. This effect can be explained by the effect of the parameters:

- nature of absorbed ions,
- concentration of ions on the surface and in the *depth* of the solid ion exchange phase and in the electrolyte solution,
- solution temperature,
- the previous *history* of the ion exchanger, expressed in the structuring of solid phase pores, as a result of the preliminary *training* of ionite,
- initial structure of ionite,
- possibility of interaction of ionite in water, and
- rate and hydrodynamic mode of solution transmission, and other possible factors under conditions of complex mixture of ions in solution, characteristic of ionite regeneration a greater extent.

In addition, instrumentation and control system including sensors, equipment diagnostics and advanced controls has a great importance [25-29]. But this question is the topic of another research, which was also conducted by authors.

Flue gas cleaning method is based on waste-water disposal. It was first developed and proposed by scientists from Kazakhstan [30].

There are no restrictions on the use of this technology. It is possible to clean flue gases not only at thermal power plants and boiler houses, but also in metallurgical furnaces and installations that burn associated gas in the oil and gas industry.

The disadvantages of the method lie in the incomplete cleaning of flue gases from SO_x and GHG, but this is the subject of further research and development to improve the method.

Subsequent research tasks include experiments for the development of a technology for the integrated treatment of flue gases and waste-water on industrial equipment in thermal power plants. Difficulties are expected due to the possibility of gypsum formation, but this process can be controlled and the effects of gypsum deposits can be avoided.

Conclusions

- The regenerative properties of solutions obtained on the basis of condensate and waste-water from thermal power plants, saturated with components of flue gases, make it possible to use them for partial regeneration of cation exchangers in water purification schemes.
- The efficiency of the regeneration of cation exchangers using water solutions of waste-water saturated with components of flue gases allows the following:

- replacement of part of the used design regeneration solutions, which will reduce the consumption of reagents for regeneration by 30%,
- reducing of water consumption for own needs of the water treatment plant by 30-35%,
- reducing of the volume of waste-water from the water treatment plant by 25%, and
- carrying out efficient cleaning of flue gases from GHG, CO_2, H_2O, and SO_x at minimum capital costs and without additional operating costs.

Calculation of the limiting calcium content is carried out taking into account the contact temperature of flue gases of 150 °C and a mixture of clarified and waste-water –20 °C. The multiplication of solubility for $CaSO_4$ is 0.2036 grams per 100 g of water or 2.036 g/dm^3 at a given temperature.

The average sulphate content in the blowdown water is 800.84 mg/m^3 at an average flow rate of 26.4 m^3 per hour.

The average value of the sulfate content in the waste-water of the anion exchange filters of the water treatment plant is 43.42 mg/m^3 with an average volume flow rate about 75.1 m^3 per hour.

The concentration of sulfates is 240.4 mg/dm^3 in a solution of a mixture of blowdown water and waste regeneration anion exchange filters with a volume flow of 14.5 m^3 per hour.

The gas purification scheme for one boiler will require: the content of sulfates SO_4^{2-}, taking into account the input of waste-water: 14.5 m^3 per hour with a concentration of 240.4 mg/dm^3 and 80.8 m^3 per hour with a concentration of 805.6 mg/dm^3:

$$(14.5 \cdot 240.4/95.3 + 8.8 \cdot 805.6/95.3) = 796 \text{ mg/dm}^3 \text{ or } 16.58 \text{ mg-eq/dm}^3 \text{ or } 8.29 \text{ mg-ion/dm}^3$$

The gas purification scheme for one boiler will require: calcium content Ca^{2+}, taking into account the input of waste-water: 14.5 m^3 per hour with a concentration of 37.7 mg/dm^3 and 80.8 m^3 per hour with a concentration of 622.9 mg/dm^3:

$$(14.5 \cdot 37.7/95.3 + 80.8 \cdot 622{,}9/95.3) = 533.86 \text{ mg/dm}^3 \text{ or } 11.12 \text{ mg-eq/dm}^3 \text{ or } 556 \text{ mg-ion/dm}^3$$

This means that the maximum theoretical value of the concentration of the formed $CaSO_4$ salts will be 533.86 mg/dm^3 (according to the minimum concentration of one of the ions), which is much less than the solubility of gypsum at a given temperature – 2036 mg/dm^3.

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