The waste-to-energy technology of the energy sector

L A Nikolaeva and R Ya Iskhakova
Department of Water and Fuel Technology, Kazan State Power Engineering University, Krasnoselskaya St., 51, Kazan, 420066, Russia
E-mail: imreginaiskh@gmail.com

Abstract. Nowadays a problem of reducing anthropogenic impact on the environment is important. In the present article a perspective method of waste-to-energy technology of the energy sector is reviewed. This article focuses on the carbonate sludge (large-tonnage industrial waste) produced by power stations that is used as a sorption material, and adsorption properties of carbonate sludge, its influence on activated sludge is considered. Sludge is a microporous sorbent which is confirmed by the sorption curves for oil products and ammonia nitrogen. The carbonate sludge increases the activated sludge volume index by improving its sedimentation properties and the efficiency of centrifugation during activated sludge dewatering due to the rupture of hydrate shells of activated sludge. Granules that can be used as a fuel are obtained at the following mass ratios: excess activated sludge - 70%, carbonate sludge - 8%, binder - 22% by weight (starch and technical lignosulfonate). The production technology of fuel granules for incineration has been developed based on the research results.

1. Introduction
The energy sector is the main one for the development of all branches of industry, transport, utilities, and agriculture since the electric and thermal energies are necessary for the production of any type of goods and services. Therefore, this industry is characterized by the highest scale of production, which inevitably leads to a significant anthropogenic impact on the environment [1, 2].

Currently, the issue of efficient waste disposal of the energy sector is a priority. The following types of waste are generated at power stations: solid (slag, ash, sludge, etc.), liquid (wastewater, chemically contaminated liquids), and gaseous (fuel combustion by-products) [3]. Therefore, the issue of developing the waste-to-energy technologies at the enterprises of the energy sector is actual, which will minimize the anthropogenic impact of the energy enterprises on the environment and increase the energy efficiency of production [4, 5].

The preparation of additional water, as well as the treatment of wastewater, generated at energy enterprises, are mandatory stages before their use and drainage into the reservoir. Traditionally, there are four stages of industrial wastewater treatment: mechanical, biological, physical/chemical, and disinfection [6, 7].

The aim of the work is to develop waste-to-energy technology to improve energy efficiency and the environmental friendliness of an enterprise in the energy sector. The technology includes wastewater treatment with dosing of carbonate sludge, sedimentation of activated sludge in a secondary clarifier, centrifugation, and molding the fuel granules for incineration with additional heat released.

Karmanovskaya GRES (state district power station) is selected as the enterprise, which has a stage of water treatment of additional water for the condensate-feed path of boilers, as well as treatment of industrial wastewater.
2. Materials and Methods

Water treatment at the Karmanovskaya GRES is carried out in preliminary treatment of additional water, including liming and coagulation, and ion exchange-chemical desalination [8]. The Karmanovskoe reservoir is a source of water supply for the station; annually, about 1 million m$^3$ of the reservoir's source water is used to compensate steam and condensate losses at the station.

During the preparation of additional water at the stage of liming and coagulation, carbonate sludge is formed. Carbonate sludge from water treatment is a large-tonnage industrial waste that has been stored for decades at the plant's sludge disposal sites. This leads to salinization of groundwater, alkalization of the soil, lands degradation etc. Therefore, despite the fact that carbonate sludge is safe (hazard class V), the issue of effective disposal of carbonate sludge is relevant for Karmanovskaya GRES.

The qualitative phase analysis of the company diffractometer D 8 ADVANCE Bruker showed the chemical composition presented in table 1 [8].

| Chemical composition | %  |
|----------------------|----|
| CaCO$_3$             | 72 |
| Mg(OH)$_2$           | 9  |
| Ca(OH)$_2$           | < 1|
| SiO$_2$              | 0.5|
| Other substances     | 17.5|

The method of gas chromatography-mass spectrometry showed that contents of humic acid in the carbonate sludge are up to 12%. The bulk density is 0.62 g/cm$^3$, humidity - 3%, ash content - 89%.

The treatment facilities of the station receive household wastewater from the state district power station, wash water, drainage water from sludge and sand sites, as well as wastewater from the nearby Energetik village.

The large-tonnage production waste – excess activated sludge, is generated at biological wastewater treatment plants [9]. Activated sludge is a complex community of microorganisms, the life of which is carried out due to the oxidation of organic substances, phosphorus and nitrogen-containing compounds of wastewater from industrial enterprises and the municipal sector [10].

In experimental studies, an excess of activated sludge from the biological treatment plant of the Karmanovskaya GRES is used. The characteristics of the sludge are studied: the moisture content of the original activated sludge is 99%, after the stage of compaction (sedimentation under the influence of gravitational forces) - 96%, density – 1.15 g / cm$^3$, ash content – 12%.

Bulk density is determined according to this method: the sorbent dried at 110 °C is poured in portions of 20 cm$^3$ into a previously weighed cylinder with a volume of 100 cm$^3$ and a height of 240 mm. The cylinder is shaken by lightly tapping the bottom on a wooden disc for 30 seconds in an inclined (70-80°) position after which the cylinder is weighed again.

The determination of moisture content method consists in drying a sample of the product to constant weight and determining the reduction in the weight of the product.

Ash content is determined according to this method: the sample is burned in a muffle furnace heated at a certain rate to a temperature of 815 °C, and kept at this temperature until constant weight. The platen is placed in a muffle furnace at room temperature. Within 60 minutes the oven temperature is raised to 500 °C and then this temperature is maintained for 60 minutes. Heating is continued to (815 ± 10) °C in the same oven and kept at this temperature for at least 60 minutes.

The concentration of ammonium nitrogen was determined in accordance with the titrimetric method using the preliminary distillation of ammonia to boric acid solution.

The residual content of petroleum products was determined using the IR spectrometric method. The method is intended for measuring the mass concentration of oil products in wastewater samples by IR
spectrometry using the AN-1 and KN-1. The range of measured concentrations of oil products is from 0.05 to 50 mg / dm³. The method consists of the extraction of emulsified and dissolved petroleum products from water with carbon tetrachloride; separation of petroleum products from associated organic compounds of other classes in a column filled with aluminum oxide and measurement of mass concentration of petroleum products by IR spectrometry.

The sludge volume index is equal to the volume occupied by 1 g of dry active sludge after 30 minutes of settling in the cylinder. A sample of the activated sludge mixture is shaken, 100 cm³ is poured into the cylinder and is precipitated for 30 minutes, then the volume occupied by the activated sludge is measured. The sludge is filtered through a pre-weighed filter and dried in an oven at a temperature of 105°C. After drying, the filter is cooled and weighed. The difference between the mass of the filter before and after determination is the dry mass of the activated sludge.

To assess the moisture yield of excess activated sludge, laboratory studies were carried out on a CM-6M centrifuge, in which the separation of the dispersed and liquid phases occurs by precipitation of suspended particles under the action of centrifugal forces. Previously, the excess activated sludge was intensively mixed with the sludge in various ratios for 5 minutes. Then the mixed sediment was placed in 10 ml centrifuge cylinders and centrifuged under various conditions.

When molding granules, starch and technical lignosulfonate (LST) were used as a binder.

The experimental determination of the heat of fuel incineration is carried out by the calorimetric method. The calorific value is the total energy released as heat when a substance undergoes complete incineration with oxygen under standard conditions. The chemical reaction is typically a hydrocarbon or other organic molecule reacting with oxygen to form carbon dioxide and water and release heat. Elemental analysis of fuel pellet substances with carbon, nitrogen and sulfur content (CHNS - analysis) was carried out on an EA 3000 EuroVector analyzer.

3. Results
The sludge has adsorption properties to various substances [11]. The ability of the sludge to adsorb oil products, ammonium nitrogen and other impurities has been established. Ammonium nitrogen and phosphates are typical for domestic wastewater entering the wastewater treatment plant from the Karmanovskaya GRES and the Energetik village; oil products enter the wastewater from the station's fuel oil facilities.

The sorption capacity of petroleum products and ammonium nitrogen was determined under static conditions. The sorption isotherms of the investigated contaminants are constructed (Figure 1).

![Figure 1. Oil products sorption isotherm.](Image)

![Figure 2. Logarithmic form of the oil products sorption isotherm.](Image)
The adsorption isotherm is of type I according to the BET classification. Therefore, the carbonate sludge contains micropores [12]. The initial portion of the curve is described by linear dependence of Henry’s law [13]. Then the curve goes to the equilibrium, which conforms to Langmuir's theory of the monolayer formation on the sorbent surface. The isotherm (Figure 2) is described by Freundlich’s equation (1):

\[ A = 0.28C^{0.75} \]  

(1)

The ammonium nitrogen adsorption isotherm is shown in Figure 3.

As the ammonia nitrogen concentration increases, the sludge saturates and reaches the sorption equilibrium. The adsorption capacity of the material for ammonia nitrogen is 3.2 mg/dm³. The sorption isotherm of ammonia nitrogen in logarithmic form is shown in Figure 4. The isotherm is described by Freundlich’s equation (2):

\[ A = 2.5C^{0.52} \]  

(2)

Therefore, the curves display the possibility of using sludge as a sorption material to improve the quality of biological wastewater treatment.

Dried carbonate sludge with constant humidity of 3% was dosed into the aeration tank. It was experimentally established that the optimum dose of injected sludge is 600 mg/dm³ [14]. The carbonate sludge can be used as a sorption material for biological sorption treatment of industrial wastewater together with activated sludge microorganisms. Such a method will combine the biochemical oxidation of impurities with activated sludge and adsorption treatment with carbonate sludge. The combination of biochemical and adsorption treatment will improve the quality of wastewater treatment.

The introduction of this dose of sludge reduces the value of the sludge volume index and the concentration of suspended solids in the clarified water to the normative values (Table 2).

The obtained values are reached after settling of wastewater in the secondary clarifier for 2 hours. Dosing of carbonate sludge makes it possible to increase the efficiency of wastewater treatment in terms of suspended solids. The formation of a biofilm on its surface contributes to the weighting of activated sludge, thereby the sedimentation properties of activated sludge are increased. The research results indicate that the maximum effect of reducing suspended solids is achieved when dosing sludge in an amount of 600-900 mg / dm³ and after the settling stage in the secondary clarifier the concentration of suspended solids does not exceed the normative values of suspended solids in the reservoir (5.65 mg / dm³).
Table 2. Change the sludge volume index and suspended solids from the injected dose of sludge.

| Dose of carbonate sludge, g/dm$^3$ | Concentration of suspended solids, mg/dm$^3$ | The sludge volume index, sm$^3$/g |
|-----------------------------------|---------------------------------|---------------------------------|
| 0                                 | 28.14                           | 141                             |
| 0.3                               | 10.11                           | 112                             |
| 0.6                               | 5.62                            | 80                              |
| 0.9                               | 5.29                            | 74                              |

After the secondary clarifiers, the carbonate sludge together with the excess activated sludge was centrifuged. Excess activated sludge and a mixture consisting of excess activated and carbonate sludge in various proportions were centrifuged. The centrifugation index was used, which shows the degree of dehydration of sludge in the field of centrifugal forces. The centrifugation index $U \leq 6-8$ is considered a satisfactory value of sludge dewatering. The centrifugation times were 1, 2 and 3 minutes. The centrifuge rotation speed was between 1000 and 1500 rpm. The research results are shown in Figure 5 and Figure 6.

![Figure 5](image1.png)  ![Figure 6](image2.png)

**Figure 5.** Dependence of the centrifugation index value on the injected sludge dose (1000 rpm) (Centrifugation time: - 1 min, ■ - 2 min, ▲ - 3 min).

**Figure 6.** Dependence of the centrifugation index value on the injected sludge dose (1500 rpm) (Centrifugation time: - 1 min, ■ - 2 min, ▲ - 3 min).

The satisfactory value of the centrifugation index (Fig. 5) ($U = 7.95$) is achieved with the introduction of carbonate sludge with a minimum dose of 0.6 g / dm$^3$ (centrifuging the sediment at a speed of 1000 rpm for 1 minute), while centrifugation of only excess activated sludge under the same conditions has a much higher index ($U = 10.05$) and is ineffective.

The satisfactory value of the centrifugation index (Fig. 6) ($U = 8.01$) in the treatment of excess activated sludge without adding carbonate sludge is achieved at 1500 rpm for 3 minutes. It is the most energy-consuming process.

After centrifugation, the dewatered mixture of excess activated and carbonate sludge was molded by hand into granules with a diameter of 3-5 mm using a binder by rolling for further incineration [15]. Granules were obtained at the following mass ratios: excess activated sludge — 70%, carbonate sludge — 8%, binder — 22% by weight (starch and LST). Then, after rolling, drying was carried out at 105 °C for 30 minutes.
Table 3 displays the general technical characteristics of the obtained granules using starch and LST as a binder: moisture, bulk density, ash content, and abrasion resistance. Calorimetric determination of the calorific value of the granules was carried out (C 2000 basic V. 1).

| Sample                        | with starch (22 % by weight) | with LST (22 % by weight) |
|-------------------------------|-----------------------------|---------------------------|
| Moisture, %                   | 4.9±0.1, 3.3±0.1.           |
| Bulk density, kg/m³           | 831                         | 792                       |
| Ash content, %                | 30.2                        | 27.7                      |
| Colour of ash                 | light grey                  | light brown               |
| Abrasion resistance, %        | 0.6                         | 0.1                       |
| Heat of combustion (MJ / kg)  | 9672.6                      | 10345.5                   |

Therefore, comparing the general technical characteristics of granules using starch and LST, as well as their heats of incineration shows that the use of granules using LST as a binder is more efficient.

An elemental analysis of this sample for the content of carbon, hydrogen, nitrogen and sulfur (CHNS - analysis) was carried out on an EA 3000 EuroVector analyzer. According to the results the fuel granules have the following composition: C = 30.1%; H = 2.9%; S = 1.1%; N = 1.24%.

Based on the elemental composition according to Mendeleev’s formula, the lower heat of combustion of the fuel can be calculated (3):

\[
Q = 339.3C + 1256H - 109(O-S) - 25.2(9H+W)
\] (3)

The lowest heat of combustion of fuel using LST as a binder will be 9582.8 kJ / kg.

4. Discussion

The obtained curves (Figure 1, Figure 3) indicate the possibility of using carbonate sludge as a sorption material to improve the quality of biological wastewater treatment.

A decrease in the value of the sludge volume index indicates the effective biological treatment systems: the activated sludge has a dense structure, there are no loose small flakes. The decrease of the sludge volume index is also explained by the alkaline nature of the sludge. The increase in the pH of the water to a weakly alkaline medium helps to reduce the growth of filamentous bacteria and allows suppressing the swelling of activated sludge. The charged Ca\(^{2+}\) ions on the sludge surface contributes to the electrostatic interaction of the material with activated sludge, which, under the condition of 4 \(\text{pH} < 9\), is considered negatively charged. Therefore, the carbonate sludge causes the conglomerate of activated sludge particles, which has a positive effect on the operation of secondary clarifiers.

Under the same experimental conditions, it was found that due to the addition of carbonate sludge, the moisture yield of excess activated sludge increases and the power input for the process is reduced. The moisture of the excess activated sludge after centrifugation is 84%, while the moisture content of the mixed wastes (excess activated and carbonate sludge) ranges from 69-71% (depending on the dose of injected sludge and the conditions of the experiment).

The chemical treatment of the sediment by adding carbonate sludge, which acts as a mineral coagulant, is proposed for improving the moisture disengagement of excess activated sludge. The introduction of carbonate sludge makes it possible to disrupt the agglomeration stability of the excess activated sludge suspension by breaking the hydration shell enveloping the sludge particles. When centrifuging activated sludge together with carbonate sludge, strong structural bounds are broken, which makes it possible to separate colloid-bound moisture. Thus, a redistribution of the bound moisture of excess
activated sludge occurs and the content of free water in the suspension increases. A significant content of Ca$^{2+}$ forms a rigid mechanical structure of the sediment, promotes electrostatic interaction with activated sludge, which in the range 4 < pH < 9 is considered as negatively charged.

The production technology of fuel granules for incineration has been developed based on the research results.

5. Conclusion
Based on the results of the research, an integrated waste-to-energy technology for the wastes disposal of Karmanovskaya GRES (carbonate sludge and activated sludge) was obtained, which includes the following stages:

- biosorption wastewater treatment using carbonate sludge;
- increasing the sludge volume index by improving the sedimentation properties of activated sludge;
- increasing the efficiency of centrifugation during sludge dewatering due to the rupture of hydrate shells of activated sludge with sludge;
- creation of granules on the basis of waste for incineration, which enables to get additional energy.

6. Acknowledgments
The study was carried out within the framework of the Russian Science Foundation grant No. 18-79-10136 «Theoretical methods of modeling and development of energy-efficient import-substituting devices for cleaning and raw hydrocarbons deep conversion at the enterprises of the fuel and energy complex.

References
[1] Nikolaeva L A and Iskhakova R Ya 2019 Adsorption of industrial wastewater from oil products with application of mathematical modeling *IOP Conf. Series: Earth and Environ. Sci.* 288 012017
[2] Medvedev V T 2002 *Inzhenernaya Ekologiya* [Engineering Ecology] (Moscow: Gardariki) [in Russian]
[3] Timonin A S 2003 *Inzhenerno-Ekologicheskii Spravochnik* [Engineering-Ecology Reference Book] (Kaluga: Izd. N. Bochkarevoi) [in Russian]
[4] Brunner P H and Rechberger H 2015 Waste to energy – key element for sustainable waste management *Waste Management* 37 3-12
[5] Lindberg D, Molin C and Hupa M 2015 Thermal treatment of solid residues from WtE units: a review *Waste Management* 37 82-94
[6] Henze M, Mark van Loosdrecht M, Ekama G and Brdjanovic D 2008 *Biological Wastewater Treatment: Principles, Modeling and Design* (London: IWA Publishing)
[7] Grady C P L, Daigger G T, Love N G, Filipe C D M 2011 *Biological Wastewater Treatment* (Boca Raton: CRC Press)
[8] Nikolaeva L A and Iskhakova R Ya 2019 Integrated Wastewater Treatment for a GRES *Thermal Engineering* 66 587-92
[9] Chang I-S, Clech P L and Jefferson B 2002 Membrane fouling in membrane bioreactors for wastewater treatment *J. of Environmental Eng.* 128(11) 336-43
[10] Muga H E and Mihelcic J R 2008 Sustainability of wastewater treatment technologies *J. of Environmental Management* 88 437-44
[11] Lupeiko T G, Gorbunova M O and Bayan E M 2004 Deep purification of aqueous solutions to remove iron (III) with carbonate-containing industrial waste *J. Appl. Chem.* 77 79-82
[12] Romankov P G and Frolov V F 1990 *Massoobmennye protessy khimichesky tekhnologii. Sistemy s dispersnyo tverdy fazy* [Mass Exchange Processes of Chemical Technology] (Leningrad: Chemistry) [In Russian]
[13] Wanga S and Peng Y 2010 Natural zeolites as effective adsorbents in water and wastewater treatment Chemical Engineering J. 156 11-24
[14] Nikolaeva L A, Laptev A G and Iskhakova R Ya 2018 Improving the efficiency of wastewater biological treatment at chemical plants Water Resources 45 231-7
[15] Parka J B K, Craggsa R J and Shilton A N 2010 Wastewater treatment high rate algal ponds for biofuel production Bioresource Technology 102 35-42