Structural and surface and acid-base properties of thermal power plant ash and slag

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The ash slags formed at thermal power plants operating in the industrially developed northern region of the Russian Federation (Murmansk region) were investigated with the methods of BET (S. Brunauer, T. Emmett, and E. Teller) and BJH (Barrett-Joyner-Highland). It was found that the material has a predominantly mesoporous structure with a pore volume in the diameter range of 1.7–300 nm equal to 0.051 cm³/g and a specific surface area of 17.8 m²/g, which corresponds to the maximum levels observed at European thermal power plants of average power. It is established that the studied ash slag samples are characterized by a bimodal distribution of particles with a predominance of a fraction of 40–64 micrometers. It is shown that by its physico-chemical and structural-surface properties, the ash-slag mixture belongs to type F according to the international classification ASTM C 618, according to which it can be recommended for direct use as a sorbent in the treatment of domestic wastewater, and the pH value of the iso-ion point (7.63) indicates a predominant sorption of cationic forms of biogenic elements on the studied sample.

Keywords: ash and slag mix, thermal power plant, structural and surface properties, acid-base properties, sorption.

Структурно-поверхностные и кислотно-щелочные свойства золошлаков тепловых электростанций

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Методами БЭТ (С. Брунауэр, Т. Эммэтт и Э. Тэллер) и BJH (Баррет-Джойнер-Хайленд) исследованы золошлаки, образующиеся на тепловых электростанциях, работающих в промышленно развитом северном регионе Российской Федерации (Мурманская обл.). Обнаружено, что материал имеет преимущественно мезопористую структуру с объёмом пор в диапазоне их диаметра 1,7–300 нм равном 0,051 см³/г и удельную площадь поверхности 17,8 м²/г, что соответствует максимальным уровням, наблюдаемым на европейских тепловых электростанциях средней мощности. Установлено, что исследованные образцы золошлаков характеризуются бимодальным распределением частиц с преобладанием фракции 40–64 мкм. Показано, что по своим физико-химическим и структурно-поверхностным свойствам золошлаковая смесь относится к типу F по международной классификации ASTM C 618, согласно которой она может быть рекомендована для непосредственного использования в качестве сорбента при очистке бытовых сточных вод, а величина поверхности pH изоионной точки (7,63) свидетельствует о преимущественной сорбции на исследованном образце катионных форм биогенных элементов.

Ключевые слова: золошлаки, тепловая электростанция, структурно-поверхностные свойства, кислотно-основные свойства, сорбция.

Coal combustion at a thermal power plant (TPP) is accompanied by the generation and subsequent storage of huge amounts of waste. According to the classification by GOST R 57789-2017 (Russia), such waste is divided into ash, slag and ash-slag mixture. According to the classification, ash is a fine-grained material with a particle size of less than 0.315 mm, while slag is a coarse-grained material with a grain size of 0.315 to 40 mm. Hereinafter we refer to ash and slag mix as ASM.

Globally, no more than 25% of TPP waste is recycled, while the recycling levels differ significantly between the world's countries [1]. The most complete recycling of TPP waste as a secondary resource is typical for the EU countries and China (90% and 67%, respectively). TPP waste, in particular ash, has traditionally found applications in the construction industry. Best global practices of TPP ash recycling in the construction industry are reviewed in [2].

Since the global consumption of thermal power plant waste by the construction industry is relatively small (10–20%), their multicomponent composition stimulated the search for other applications: extraction of aluminum, noble and rare earth elements from them, etc. [3–5]. TPP ash is also used in the production of zeolites, geopolymers, ceramics, etc. [6]. TPP ash is widely used in agricultural activities as a reclamation additive [7, 8].

The morphology of coal ash, its high specific surface area, porosity, multicomponent chemical composition, characterized by the presence of SiO_2, oxides of Fe, Al, Ca, and etc., contribute to the active development of its applications in water treatment as a coagulant and sorbent [9]. Ash and slag are considered as an economically viable alternative in those areas of water treatment, where activated carbons and ion exchange resins have been traditionally used [3]. The presence of unburned carbon residue in ash and slag makes it possible to recover from wastewater such organic compounds as dyes, phenols, herbicides, petroleum products, polychlorinated biphenyls, as well as radionuclides and heavy metals [1, 10].

A review of the existing methods for recovery of mesoporous sorbents from TPP ash and their applications is given in [1]. This paper also presents the main methods for the analysis of ash and its modified forms. The assessment of the prospects of using coal ash in water treatment is based on such key properties as particle size distribution, specific surface area, hydrophilicity, porosity [11, 12].

At the end of the 20th century, ASM stockpiles in the Russian Federation occupied an area of 20 thousand hectares and held approximately 1.3 billion tons of waste with an average annual increment of ≈ 50 thousand tons [13]. A review of existing research and patent search showed that in Russian literature, little is known about the applicability and state of knowledge on ash and slag as potential sorbents for wastewater treatment. However, this is an extremely urgent problem, in particular, in connection with the wider use of the shift method in the development of the Russian Arctic. In the Arctic, building large water treatment facilities using conventional processes for deep biological treatment of household wastewater to remove biogenic elements (nitrogen and phosphorus) is not economically feasible. Sorption treatment methods using ore mining waste or local TPP waste can be an alternative for water treatment at small treatment plants operated at shift camps.

Search for sorbents is currently underway, the use of which in the processes of removing biogenic elements from household wastewater is permissible without subsequent regeneration of the waste material, which should be compatible with disposal in soil [14, 15]. A mixture of ash and slag and sorbate could be an ameliorant with a prolonged fertilizing effect on nitrogen, phosphorus, silicon, potassium, calcium, magnesium, as well as a wide range of trace elements remaining both in coal ash and in household wastewater.

The purpose of this work was to determine the physico-chemical properties of the ash-slag mixture (granulometric composition, structural-surface and acid-base properties) to assess the possibility of their applicability as a sorbent in the treatment of domestic wastewater.

Objects and methods of research

Sampling. The object of research was the fresh ash and slag sampled from the active ash stockpile at the Apatity Thermal Power Plant in Murmansk Region, Russia. The TPP primarily runs on the coal from the Inta, Kuznetsk, and Khakass deposits and uses fuel oil as a starting fuel. The surface area of the active ash stockpile is 20 hectares. Sampling of the ash and slag mixture was carried out in the reclamation zone according to Russian national standard GOST R 57789-2017 (in Russia) as a combined sample of ten point samples, at a depth of 20 cm. Each point sample weighed 4–5 kg. For testing, the combined ASM sample was thoroughly mixed

and then averaged by quartering to obtain a laboratory sample.

ASM chemistry. To measure the gross content of macronutrients (Si, Al, Fe, Na, Ca, Mg, K, P, etc.), a 200 mg sample of the ASM was subjected to open acid decomposition with a mixture of HNO_3, HF, HCl in glass-carbon crucibles. To remove hydrofluoric acid, sulfuric acid was added and the resulting mixture was distilled to thick white vapor. HNO_3, HF, HCl acids first underwent isothermal distillation in a Berghof (Germany) unit. After decomposition, the solutions were transferred into polypropylene 50 or 100 ml tubes, which were filled to the mark with a 2% HNO_3 solution. A 2% HNO_3 solution was also used to dilute the solutions. Deionized water was obtained using a Millipore Element water purification system (by Millipore, USA).

Analysis was performed using an ELAN 9000 DRC-e inductively coupled plasma mass spectrometer (by Perkin Elmer, USA). To tune the instrument, we used a Multi-element ICP-MS Calibration Standard STD 1 sample (by Perkin Elmer); to calibrate the instrument, we used the standard solutions ICP-MS Calibration Standard IV-STOCK-21 and IV-STOCK-29 (by Inorganic Ventures, USA) with a mass concentration of the measured elements of 10 mg/dm³. The measurement error did not exceed 0.5% at $P = 0.95$.

ASM physical and chemical properties. ASM particle size distribution was measured using a sieve analyzer in accordance with GOST 12536-2014 (Russia).

X-ray phase analysis (XRD) was performed using a SHIMADZU XRD-600 instrument with an angle range of 2Θ from 6 to 70° with an increment of 0.02°. The phase composition was identified using the International Diffraction Database JCPDC-ICDD 2002.

The structural and surface properties were examined using a TriStar 3020 specific surface area and porosity analyzer by the BET and BJH methods.

Acid-base properties of the ASM surface. The pH of the ASM aqueous extract was determined according to GOST 27753.3-88 (Russia) at a soil to water sample ratio of 1 : 5.

The acid-base properties of the ASM surface were investigated by discontinuous titration of the suspension to determine the pH value of the isoionic point (IIP) (pH_{IIP}) [16].

To determine the value of pH_{IIP}, the pH values of distilled water were determined with pH_o from 1 to 10 (pH_o), before and after contact with the test samples. Different acidity of distilled water was achieved by adding certain amounts of a 0.1 M HCl or KOH solution. Samples ASM weighing 0.4 g were placed in tubes and 30 mL of distilled water was added. After that, the suspension was stirred on a laboratory shaker for 2 hours to achieve adsorption-desorption equilibrium. Then the suspension was filtered and the pH of the filtrate (pH_{fin}) was measured.

Based on the difference in the acidity values of the solution before adsorption (pH_o) and after adsorption (pH_{fin}), the change (ΔpH) was found as a result of hydrolytic adsorption as follows:

$$\Delta pH = pH_o - pH_{fin}$$

The intersect between the $\Delta pH \sim f(pH_o)$ curve for the test sample with the x-axis is the value of pH_{IIP}, and the slope tangent is the exchange capacity (EC) of the surface groups of the material.

Each experiment was repeated 3 times. The measurement error did not exceed 2% with a confidence probability of $P = 0.95$.

Results and discussion

ASM chemistry. Based on the chemical analysis, silicon and aluminum oxides predominate in the ASM and a high content of iron, calcium, and magnesium oxides is observed (Table 1).

International practice has adopted the ASTM C 618 standard for the classification of thermal power plant ash [17], based on its content of basic oxides. If the content of SiO_2, Al_2O_3 and Fe_2O_3 in total exceeds 70%, the ash is classified as F-type, which the most suitable for use in water treatment. Ash is used there in three main roles: adsorption, filtration, and coagulation. In the first case, the decisive factor is the content of the carbon residue, in the second one of SiO_2 and Al_2O_3, in the third one of Al_2O_3 and Fe_2O_3. The prediction of the sorption properties of TPP waste is also carried out based on the ratio of SiO_2/Al_2O_3. Their use as a sorbent is recognized as promising at values of this ration exceeding 2.4 [12]. The gross content of SiO_2, Al_2O_3 and Fe_2O_3 in ASM in total exceeds 76%, and the

Table 1

Chemical composition of ASM, %

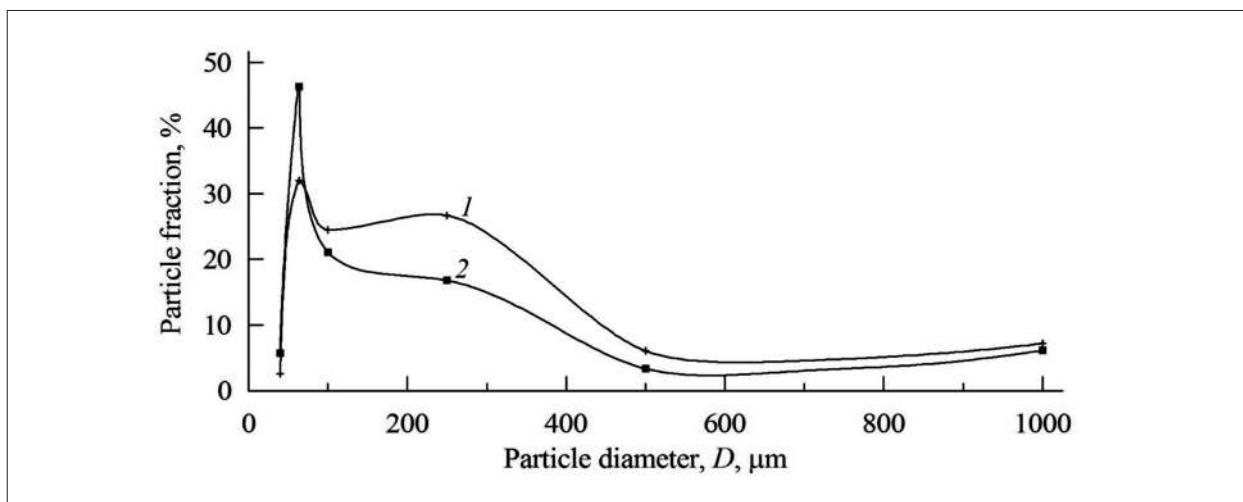| Na₂O	MgO	Al₂O₃	SiO₂	P₂O₅	SO₃	K₂O	CaO	TiO₂	MnO	Fe₂O₃
0.6	2.9	23.3	47.9	0.8	1.0	1.0	2.1	1.2	0.1	5.8

Fig. 1. Particle size distribution of the ASM The line number corresponds to the sample number

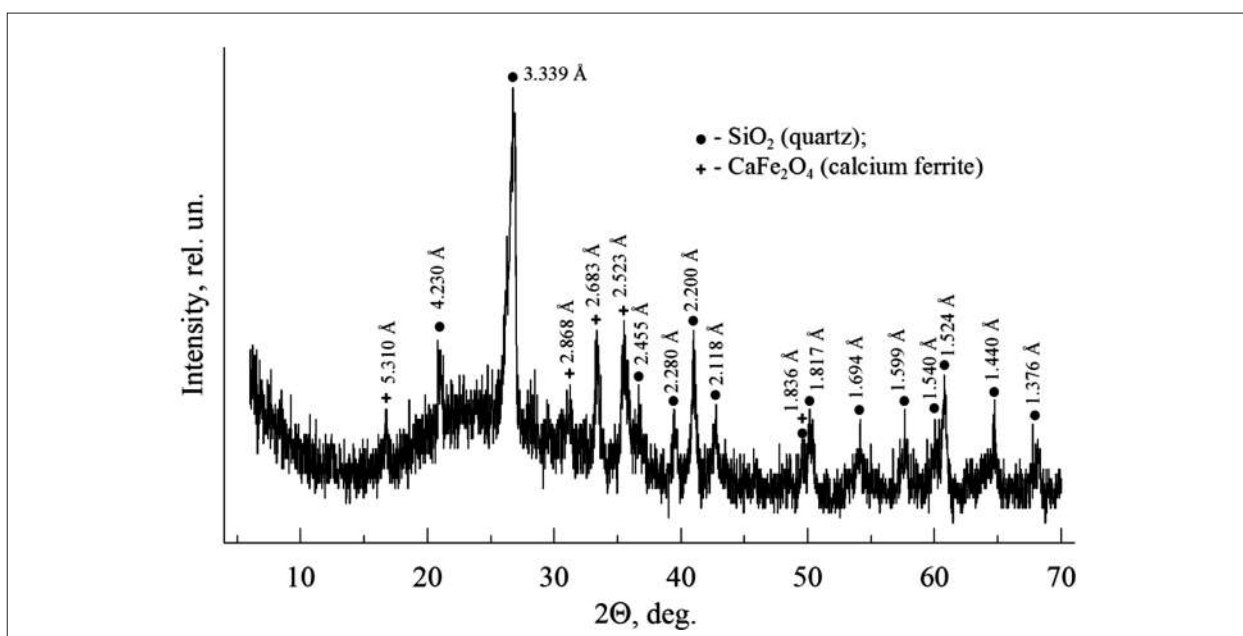**Fig. 2.** X-ray diffractogram of ASM

ratio of SiO_2/Al_2O_3 is 2.06, therefore these can be considered for use in sorption wastewater treatment processes.

ASM particle size distribution. In terms of particle size distribution, the ASM used in the experiments belongs to the silty sand fraction, with the particle size distribution curves for two close sampling points shown in Figure 1. The particle size distribution of TPP waste depends on the mineral composition of the feed coal. In large-scale studies of the ash from the TPPs operated in Europe, in most cases, a regularly shaped particle size distribution curve with a maximum in the range of 10−30 μm was observed. However, in some cases, the distribution was asymmetric or bimodal with a maximum

at 100 μm [18]. As can be seen in Figure 1, the ASM is characterized by a bimodal distribution with a smoothed second maximum. ASM is dominated by the 40−64 μm fraction, which can be explained by the presence of slag. The greatest variability of the particle size was noted in the range of 100−400 μm, which is probably due to the difference in the content of the coarse glass phase in the samples taken.

ASM phase composition. Based on the XRD data (Fig. 2), two mineral components are clearly identified in the analyzed sample – quartz (SiO_2) (record 33−1161 in the International Diffraction Database JCPDC−ICDD 2002) and calcium ferrite $(CaFe_2O_4)$ (record 32−0168). No other phases $(Al_2O_3$, CaO, MgO, etc., or

compounds thereof) were found. This can be explained by their presence in the sample in an X-ray amorphous state.

TTP ash usually has a rich mineral composition dominated by quartz, hematite, magnetite, mixed silicates of Al, Ca, Na, and potassium oxide. Analysis with the use of highly sensitive equipment identified in the ash samples 316 individual minerals and 188 groups of minerals [11]. However, up to 65% of the ash mass is in an amorphous state and is difficult to identify [19].

ASM porosity. It is currently recognized that materials with a mesoporous structure and a regular pore structure are the most promising for water treatment [1]. Figure 3 shows the nitrogen sorption-desorption isotherm for the ASM sample. The isotherm can be classified, according to the Brunauer, Deming, Deming, and Teller (BDDT) classification, as a Type IV isotherm [20, 21], which is associated with capillary condensation in mesopores, as evidenced by a pronounced hysteresis loop, whose main cause is capillary condensation of nitrogen (adsorbate) in mesopores ($2 < d_{pore} < 50$ nm). The initial portion of this isotherm is similar to a Type II isotherm. The origin of the straight middle section of the isotherm is usually used to determine the relative pressure, at which the adsorption of the monolayer is completed. The characteristic closure of the hysteresis loop on the isotherm during desorption before the relative pressure reaches 0.3, as well as the absence of a significant increase in adsorbed nitrogen in the pressure range $P / P_S < 0.1$, indicates the absence (or insignificant amount) of micropores ($d_{pore} < 2$ nm) in the ASM.

ASM pore volume distribution by diameter is shown in Figure 4. The presented findings

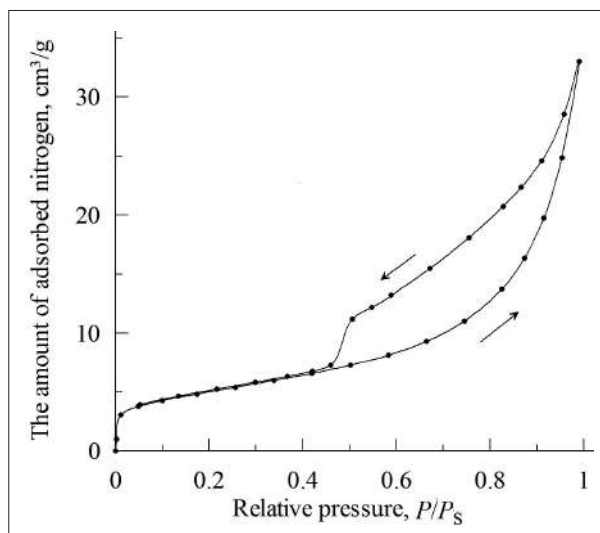**Fig. 3.** ASM sorption-desorption isotherm
$\rightarrow$ – sorption; $\leftarrow$ – desorption

support the conclusion about the mesoporous nature of the sample made above on the basis of the sorption-desorption isotherm (Fig. 3). The histogram shows that the share of micropore volume ($d_{pore} < 2$ nm) in the sample does not exceed 1%, and the fraction of macropore volume ($d_{pore} > 50$ nm) is $\approx 15\%$. Thus, based on the pore volume distribution, the ASM sample can be classified as mesoporous substances ($2 < d_{pore} < 50$ nm) – according to the classification proposed by M.M. Dubinin and adopted by IUPAC.

Structural and surface properties of the ASM are given in Table 2. BET specific surface area is a generally recognized parameter for predicting the sorption properties of a material. In the European studies of TTP ash, the value of this parameter varied between 1.3 and 12.4 m^2/g [18]. The differences are as-
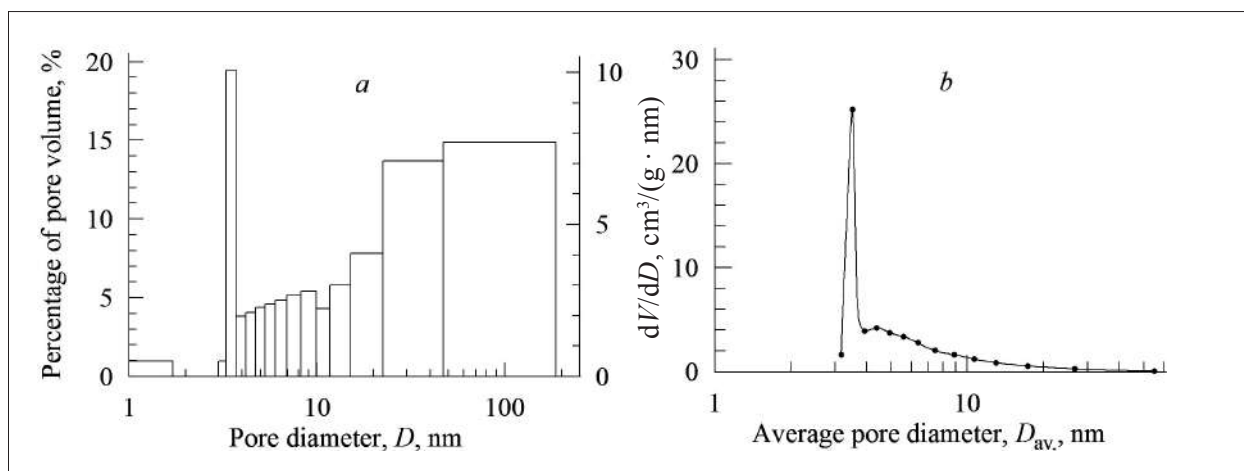

Fig. 4. ASM pore volume distribution by diameter (desorption branch) (a) – Histogram; (b) dV/dD – $D_{av.}$

Table 2

Structural and surface properties of the ASM

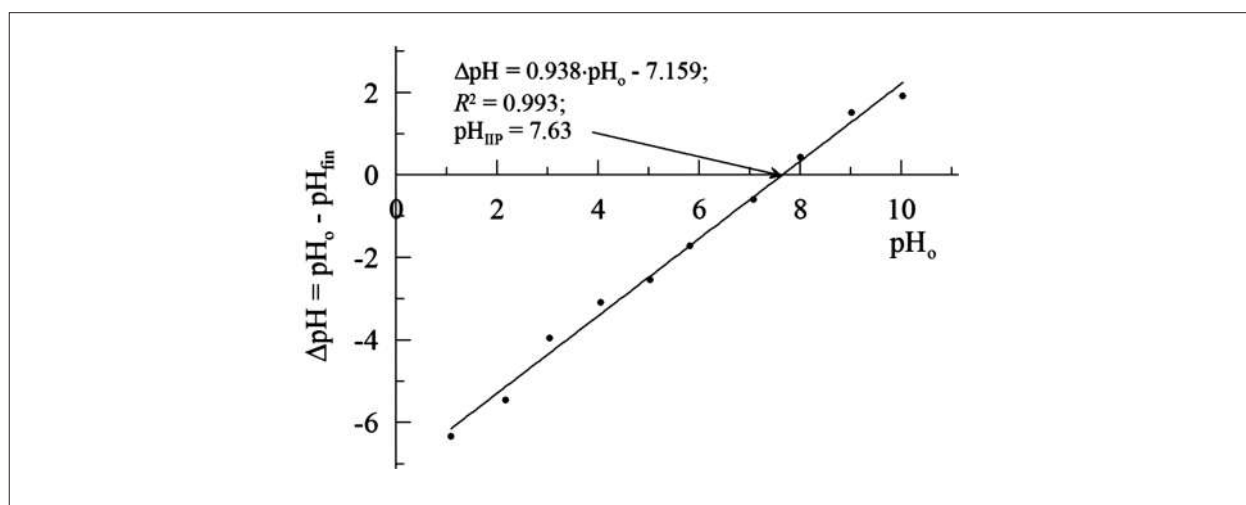| Indicator	Value
BET specific surface area, m²/g	17.80
Specific surface of micropores (d < 1.7 nm), m²/g	1.15
Specific external surface, m²/g	16.66
Specific volume of micropores (d < 1.7 nm), cm³/g	0.0005
Specific pore volume (1.7 nm ≤ d ≤ 300 nm) by the BJH method (desorption branch), cm³/g	0.0513
Average pore diameter by the BJH method (adsorption-desorption), nm	9.18

Fig. 5. ΔpH vs. pH_o of the ASM suspension

sociated with the content of unburned carbon residue, which has a very high specific surface area, comparable to the values observed in activated carbon (500–700 m²/g and higher). In the examined ASM sample, the BET specific surface area (17.8 m²/g) matched the observed European maximum.

Acid-base properties of the ASM surface. Figure 5 shows the shape of the ΔpH vs. pH_o curve for the ASM sample suspension. This shape is typical for a polyfunctional surface free of adsorbed impurities, whose degree of dissociation would exceed the dissociation of active centers of the solid itself, thereby changing the chemical equilibrium on the surface [16].

Based on the $pH_{ИP}$ one can predict the preferred direction of extraction of ions from the solution when using the ash and slag as a sorbent. If the pH of the aqueous extract is higher than $pH_{ИP}$, there is a predominant extraction of cations from the solution, and if it is lower, then the surface is positively charged, and the material acts as an anion exchanger [22]. As follows from Figure 5, $pH_{ИP}$ of the studied sample is 7.63. The pH value of the aqueous extract of the sample varies in the range of 7.73–7.93. Hence, one can

expect the predominant sorption of cations by the studied sample.

Summary

The ash-slag mixture of Apatitskaya TPP (Murmansk region, Russia) studied by BET and BJH methods is a mesoporous substance – the proportion of micropores does not exceed 1%, and macropores – 15%.

In terms of structural, surface, and physicochemical properties, TPP ash and slag mixes belong to the Type F in the international classification ASTM C 618, which makes it possible to recommend these for direct use as a sorbent in the treatment of household wastewater.

TPP ash and slag mixes can be recommended for the preferential extraction of cationic forms (for example, ammonium, which is one of the most common pollutants responsible for the eutrophication of reservoirs [23]) in sorption treatment processes at small treatment facilities.

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