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PHYSICO-CHEMICAL PROPERTIES AND POSSIBLE APPLICATIONS OF SEWAGE SLUDGE COMBUSTION ASH

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Abstract. The main problems and prospects of water disposal systems of such a megalopolis as Saint Petersburg are considered. Methods for processing sewage sludge to an ecologically safe state, as well as the use of sludge combustion ash at the Central Aeration Station (CAS) in Saint Petersburg are proposed. Special attention is paid to the issues of sludge management in the sewage system of domestic wastewater. Modern methods of physico-chemical and chemical analyses were employed to evaluate the composition and physico-mechanical properties of sludge combustion ash in the fluidised bed of the French "Pyrofluid" furnaces. The X-ray diffraction, X-ray phase and elemental analyses of the ash from the combustion of sewage sludge were carried out, the results of which allowed to infer the relationship of elemental and phase compositions of the ash to various silicate materials intended for construction and agriculture. The possibility of using ash for extinguishing and eliminating oil spills at the CAS was confirmed experimentally in comparison with similar capabilities of marshalite and fine-grained construction sand. A method for preparing dry building mixes based on Portland cement for obtaining low-water demand construction binders is proposed.

Keywords: municipal solid waste, sewage, sludge, combustion ash, treatment plant.

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Introduction

One of the most important tasks of the state is to protect the health of its citizens and improve their quality of life. It is especially relevant in large megacities. Fulfilling these tasks is only possible by implementing a whole range of different measures, among which a special place is given to the problems of water supply and sewerage. In Saint Petersburg, the "Scheme of water supply and sewerage of Saint Petersburg", created in accordance with the provisions of regulatory documents, was approved to ensure uninterrupted water supply as well as water disposal and high-quality wastewater treatment [1].

Recently special attention is paid to the implementation of innovative treatment technologies: deep removal of phosphorus and nitrogen, post-treatment and sanitation of wastewater. First, the completion of the relevant works at the Central Aeration Station (CAS) [2] and Northern Aeration Station (NAS) is planned, and further on - at all sewage treatment plants (including the South-western treatment facilities, as well as the facilities in Pushkin, Zelenogorsk, Kolpino, and Pontonny). Additionally, plans include not only sanitation, but also the utilisation of sewage sludge to an environmentally safe state. These plans concern primarily the "Severny" and "Volkhonka" landfills.

By building and launching new modern facilities for high-quality wastewater treatment, it will be possible to achieve a favourable environmental situation in the sea area of the Gulf of Finland. This is important for the fulfillment of international obligations, in particular - the recommendations of the Baltic Marine Environment Protection Commission [3]. Due to this, the study of physical and chemical properties and the identification of consumer trends in ash disposal by burning sludge is not only a scientific task.

Sewage sludge of wastewater contains almost the entire periodic system of elements. Since 60-70 wt.% of its solid phase is organic, it is possible to use it in the national economy after applicable preliminary processing. Organising industrial sites that process this kind of waste, however, requires significant capital investments for the development and implementation of technologies, operation of equipment, solutions to emerging secondary environmental problems, *etc*. In addition, since these technologies are quite complex and knowledge-intensive, almost all

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previously of the proposed solutions are applicable to processing only small amounts of waste [1].

It is a well-known fact that landfills emit unpleasant odours. Case in point: in December 2017, well drilling used to monitor the environmental condition of the “Kupchino” landfill (St. Petersburg) showed that in the adjacent territories the maximum permissible concentration for hydrogen sulphide (25 TLV) and mercaptan (1.3 TLV) in the air was exceeded. During the international seminar on the treatment and disposal of sewage sludge from urban wastewater treatment plants organised in 1993 by the State Unitary Enterprise “Vodokanal of Saint Petersburg”, specialists discussed prospects for the development of the industry, the worldwide experience in the treatment and disposal of sewage sludge, and developed recommendations for large cities and small settlements. In particular, it was noted that the neutralising technology of sludge combustion is preferable for large treatment complexes (in megacities) [3]. Regardless of the wide variety of technologies for the disposal of sludge in the world, they can be divided into two categories: thermal drying and combustion. Each method has both advantages and disadvantages [1,3]. Thermal drying allows preserving organic substances that are valuable components of fertilisers. Accordingly, this property is a serious argument in favour of this method [4,5]. Combustion can significantly reduce the total amount of sludge but, at the same time, it converts organic substances into volatile combustion products. It is also necessary to prevent the fermentation of the sludge before combusting it, since the mineralisation of some organic substances caused by this process leads to a decrease in its calorific value and, as a result, to additional and unjustified fuel costs [6,7]. Thus, in the segment of high-temperature oxidation technologies, the issues of utilization of ash from sludge incineration remain unresolved, as well as the study of the relationship of the elemental and phase compositions of ash with various silicate materials intended for construction and agriculture which became the goal of this study.

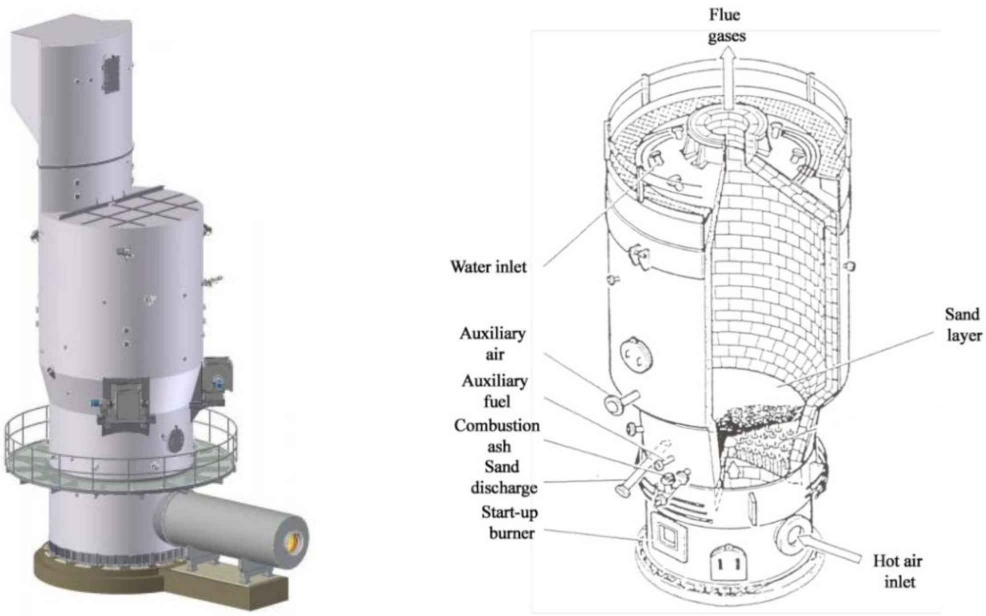
Experimental

In the Russian Federation, the “Pyrofluid” sludge combustion technology (in a fluidised bed) by OTV (France) is widely used. It is distinguished by the fact that the calorific value of the sludge itself supports the combustion process, obviating the need for additional fuel supply [4]. This was the decisive factor in the design, construction and operation of the new sludge-processing complex at the Central Aeration Station in St. Petersburg [2].

The design of the combustion furnace (Figure 1) is quite simple: a three-chamber metal structure made of shells, h_{ext}= 12 m, d_{max}= 7.5 m. The lower cylinder is the blast chamber - the upper one is the reactor. The middle part with a layer of sand is a truncated cone.

Samples description

Samples for research were averaged by “quartering” from 10 batches of ash obtained at different times.



(a) ***(b)***

Figure 1. Representation of the “Pyrofluid” furnace *(a)* and its sectional schematic view *(b)*.

Characterization methods

To determine the phase composition, an *X-ray diffraction analysis* was performed using an XRD-6100 diffractometer (Japan) combined with a computer. The JCPDS file of the International Diffraction Data Centre (ICDD) was used to decipher the recorded diffractograms [4,5].

Elemental analysis was performed on CHNS / O 2400 Series II analyser (Perkin Elmer).

Characterization of the construction binders with the obtained combustion ash was performed by determining the compressive strength, bulk density, dispersity, fire extinguishing capacity and absorbency of diesel fuel (DF), by using the universal testing machine AGS-50kNX (Shimadzu), the Analyzer VT-1000 according to previously described methods [8].

The fire extinguishing capacity of the experimental DCP was determined in accordance with the State standard (GOST) R 53280.4-2009 for the model fire centre B55 (scale 1:10) [9,10].

Results and discussion

The sewage sludge (cake) is released from the water in the sand, due to its almost instantaneous evaporation. The remaining product enters the reactor heated to 1200°C. The complete combustion of organic components of the sludge is the determining factor in ensuring the time of its stay in the reactor. The combustion process is finalised by the removal of mineral residues through flue gases in the form of ash.

When exposed to heat, cake - the dehydrated sludge - contains approximately 300 g of two-component dry matter (DM) per 1 kg, including mineral (characterised by the ash content of AC) and mostly volatile substances (VM= DM-AC). The composition of volatile substances allows determining the elements released during the combustion of the sludge. Based on the proportion of dry matter, it is possible to estimate an approximate indicator of LV of 70%. volatile matter contains are carbon, hydrogen, oxygen, nitrogen and sulphur (Table 1). Predominant organic composition of the VM indicates the possibility of oxidation (combustion). The corresponding elements of the sewage sludge are of particular importance, as they affect its lower calorific value and can be found by calculation [8].

Combustion is accompanied by the formation of flue gases, as well as ash in the form of dust - an aerosol, a highly dispersed mineral sand. The presence of the former is caused by an excess of air that oxidises VM, and the latter - by mineral substances [3]. A typical equation of the combustion process of the mass of VM with the gross formula of $C_5H_7O_2N$:

$$C_5H_7O_2N + 5.75\ O_2 = 5\ CO_2 + 3.5\ H_2O + 0.5\ N_2$$

The resulting ash can be further recycled only in the case of mono-combustion or when incinerating sludge in a mixture of ashes containing high levels of biogenic elements, such as phosphorus. Notably, the addition of solid municipal waste during incineration dramatically reduces the level of phosphorus in the ash or, conversely, it can increase the proportion of hazardous components, so that its further utilisation is impossible and the ash is neutralised by burial. Practically unique in this regard is the production of cement, where ash from the incineration of sludge is included in the product [9,10]. By calculation and experimental methods, ash from the combustion of sewage sludge (CSA) is classified as a low-hazard waste of class 4 [1]. Thus, it becomes possible to identify consumer trends and the potential of ash utilization products through the prism of its physical and chemical properties.

The X-ray diffractograms of the ash and the results of its processing along with the recalculation of the content of its elemental composition into oxides, being that it is mainly these components that form the “ash” during the combustion process at sufficiently high temperatures (up to 1250°C), are presented in Table 2.

Table 1

The elemental composition of the sludge (mass fractions).

Elemental composition	*wt. %*
C	54.16 – 56.54
H	7.37 – 7.60
O	25.46 – 28.29
N	7.28 – 8.74
S	1.09 – 1.60

Table 2

Chemical composition of CAS ash (calculated).

Oxides	*Content, wt. %*	*Oxides*	*Content, wt. %*
SiO_2	40.87	ZnO	0.50
Fe_2O_3	17.38	CuO	0.14
CaO	12.23	Cr_2O_3	0.09
P_2O_5	10.07	SrO	0.08
Al_2O_3	9.05	ZrO_2	0.08
K_2O	4.40	PbO	0.04
SO_3	2.42	NiO	0.02
TiO_2	2.11	Y_2O_3	0.01
MnO	0.51	MoO_3	0.01

Consequently, they may not be taken into account when determining possible areas of practical use. What matters is that there are no elements among them harmful to warm-blooded organisms (Table 3).

Table 3

The elemental composition of the CAS cake and ash.

Element	*CAS Cake, mg/kg*	*CAS Ash, mg/kg*
Al	39000	41000
Fe	34000	36000
Cd	8.3	11
K	18000	38000
Ca	74000	15
Co	10	11000
Mg	17000	1300
Mn	690	360
Na	3400	2800
Ni	38	45
Hg	0.05	0.05
Pb	46	51
S	8600	3200
P	58000	43000
Cr	53	85
Zn	920	1100

Among the elements whose content exceeds 1% by weight, in addition to silicon, Al, Fe, Ca, P, K, S, and Ti are presented. Their total amount in the CAS ash exceeds 90% by weight. Based on the conditions of the genesis of the studied product (T≥ 12500), they are present most likely in the form of simple and complex oxides.

The resulting X-ray diffractogram of the ash is shown in Figure 2 (the upper spectrum of the figure); the lower part shows X-ray diffractogram of the most probable phases as per the ICDD database. A comparison between the upper and lower parts of the figure indicates a highly complex composition of the sample under study. Summing up the results of X-ray spectral and phase analyses, it can be concluded that the composition of ash (elemental and phase) is related to the composition of various silicate materials for construction and agricultural purposes [6], furthermore, its unique physical and chemical properties suggest the possibility of its use for extinguishing and collecting oil spills [7,8] as well as for the recultivation of municipal solid waste landfills.

Characterization of the obtained dry building mixes based on Portland cement

Preliminary studies have confirmed the viability and potential of using ash from sludge combustion both as a fire extinguisher and as a sorbent for oil and petroleum products, as well as for use in the production technology of low-water demand Portland cement (PC) compositions (Figure 3). It is extremely interesting to find a decrease in water demand when mixing dry mixtures of Portland cement binders with CAS ash from 0.32 to 0.21.

The presence of elements such as P in the material composition of the ash and its high dispersion (*d*≈ 100 μm) determine both its sufficient fire-extinguishing capacity (extinguishing model fires of class B55 (M= 1-10) and its high absorption capacity in the elimination of oil spills (Table 4).

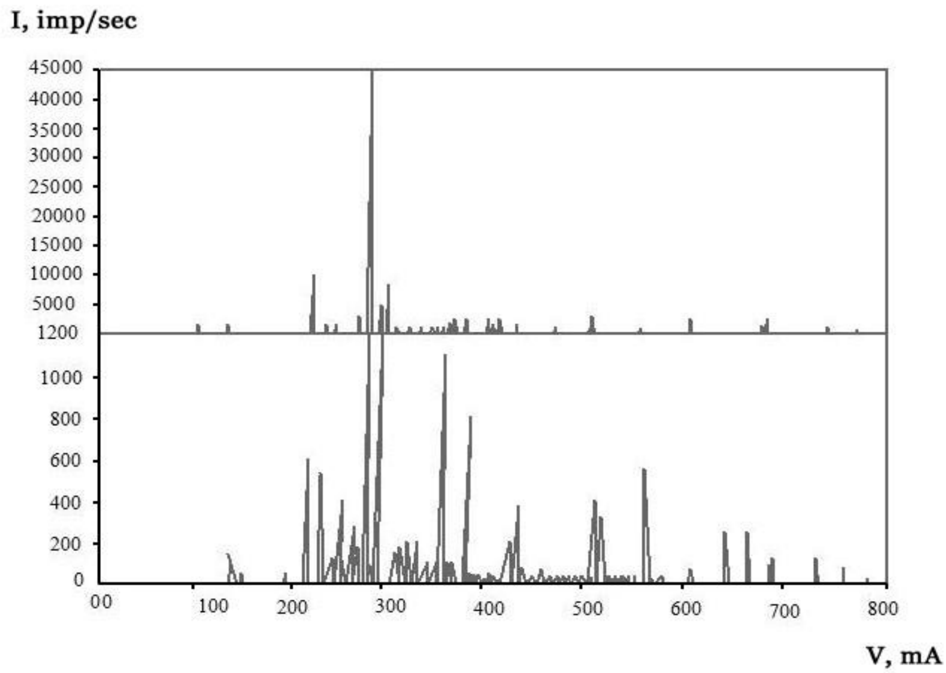


Figure 2. The X-ray diffraction data collected for CAS ash.

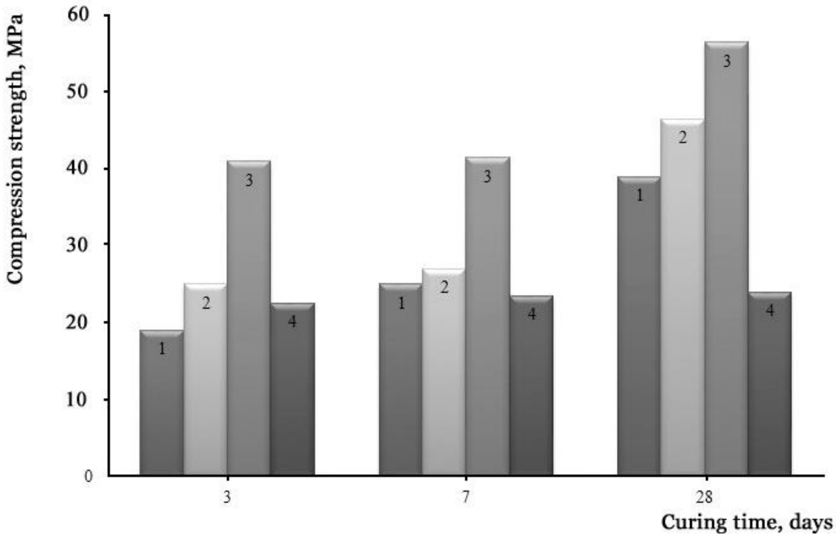


Figure 3. A histogram illustrating the increase in compressive strength of various formulations of construction binders mixed with combustion ash: PC400 - *1*; PC500 – *2*; 75%PC400+25%CC - *3*; 50%PC400+50%CC - *4*. (where, PC – Portland cement, CC – CAS ash)

Table 4

Comparative characteristics of CAS ash, marshalite and construction sand (class II; group – fine) as potential fire extinguishing powder formulations and experimental absorbents of DF spills.

Component	*Bulk density, Δ, kg/m³*	*Dispersity, $D_{medium}10^{-3}m$*	*Fire extinguishing capacity, kg/m²*	*Absorbency of DF per m³/m³ of layer*
CAS ash	750	50	≤ 0.72	0.40
Marshalite*	1150	70	≤ 0.81	0.24
Construction sand	1560	150	≤ 1.00	0.19

**Marshalite is the SiO_2 used for construction.*

It is important to note that the fire extinguishing capacity of standard dry chemical powders is within the normalised index - < 0.8 kg/m² [11-17].

Significant values of DF absorption by a layer of the studied powders showed the possibility of their use for liquidation of liquid hydrocarbon spills after extinguishing a fire. The powerful geobotanical potential of ash as a potential means of increasing the effectiveness of measures for the reclamation of MSW landfills as well as a mineral fertiliser and soil-structuring component has been revealed, but requires further study. It is obvious that ash will find its place as an additional ingredient, primarily in the technology of silicate materials. The presence of phosphorus and other biogenic elements in the ash justifies the search for ways to use it in agriculture as mineral fertiliser or soil improver.

Conclusions

The presence of elements in the combustion ash that inhibit the development of radical chain reactions of combustion, unique thermophysical properties (for example, the endo-effect of polymorphic transition in silicon dioxide) and high dispersion suggest the possibility of its use for extinguishing and collecting oil spills.

Using the methods of X-ray spectral and X-ray phase analyzes, it was shown that the composition of ash (elemental and phase) is similar in composition to various silicate materials for construction purposes, as well as unique physical and chemical properties suggest the possibility of its use for extinguishing and collecting spills of oil products, as well as for the recultivation of municipal solid waste landfills.

It is shown a decrease in water demand when mixing dry mixtures of Portland cement binders with CAS ash from 0.32 to 0.21.

The presence of elements such as phosphorous in the material composition of the ash and its high dispersion ($d \approx 100$ μm) determine both its sufficient fire-extinguishing capacity and its high absorption capacity in the elimination of oil spills.

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