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Catalytic Combustion of Wastewater Sediments from Community Facilities

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Abstract

A process was studied concerning the combustion of municipal wastewater sediments from sludge fields of the Gorvodocanal Co. (Novosibirsk), in the fluidized bed of a catalyst. It was found that at the process temperature of 700 °C, the burnout level of the sediment amounted up to 98 %. In this case, the content of toxic substances (Hg, HCl, SO₃, P₂O₅, CO, NO_x meets the sanitary standards. It was demonstrated that the combustion of sediments is possible after its preliminary drying up to obtaining the moisture level equal to 54 %.

Key words: catalytic combustion, fluidized bed of catalyst, wastewater sediments from community facilities

INTRODUCTION

Every year at the treatment plants of community facilities in Russia there are more than 2.5 million tons of sediments formed (calculated for dry solid) [1]. Wastewater sediments (WWD) are formed after the primary physical-chemical treatment and secondary precipitation after the biological treatment (activated sludge); it represents a paste-like organic mass with the moisture content of about 98-99%. Dry solid matter is within 40%composed of mineral compounds and within 60 % it is composed of organic matter presented by carbohydrates, proteins, fats, lignin, tannins and other compounds. Despite the fact that the most part of the sediment is naturally occurring, its composition includes mineral and organic compounds of man-caused origin. This could be explained by the specificity of urban sewerage systems, wherein mixing occurs urban and industrial wastewater occurs. There are heavy metal compounds, organic compounds such as benzpyrene, pesticides, polychlorinated biphenyls, phenols, etc. Many compounds exhibit mutagenic activity. In addition, sediment, including activated sludge represents a living substrate, an accumulation of various microorganisms and protozoa, which makes a hazard of parasitic infecting a human organism [2]. In this connection, the use of such sediments in agriculture is very problematic [3].

The main method used for the neutralization of such sediment, both in Russia and abroad, consists in their storage and subsequent disposal. However, due to a high humidity of the sediments, their storage occupy vast territories. Currently used ranges for the disposal of sediments, for example in Novosibirsk, are spent, whereas sludge beds operate in an overburden mode. As the result of using the range, toxic compounds and heavy metals are accumulated in the soil; mobile species of heavy metals are leached into the underground water. It is rather possible that toxic substances enter into the atmospheric air with dust.

A more reliable method for the disposal of sediments consists in their high-temperature combustion, for example, in layered furnaces, flare furnaces, furnaces with a fluidized bed of inert materials such as sand [4]. However, these processes are accompanied by secondary pollution by toxic products of high-temperature combustion (CO, NO_x , SO_x , benzpyrene species, *etc.*).

The Boreskov Institute of Catalysis, SB RAS, has developed a novel method for the lowtemperature combustion of various fuels and wastes in a catalyst fluidized bed of [5], in order to eliminate the most part of the disadvantages of high-temperature incineration. In particular, at the humidity level of sediments less than 75 % the process could be carried out in an autothermal mode, *i.e.* without the consumption of additional fuel, with more than 15-fold reducing the size and the metal consumption of units, with eliminating or crucially reducing the formation of gaseous emissions contaminated with toxic organic substances, carbon, nitrogen and sulphur oxides [6].

This paper presents the results of studying the catalytic combustion of wastewater sediments from the sludge fields of the Gorvodocanal Co. (Novosibirsk).

EXPERIMENTAL

In the course of the experiment, we used wastewater sediment from sludge beds of the Gorvodocanal Co. preliminary dried at 120 °C during 4 h. The initial moisture content in the sediment was equal to 52 mass %. In order to study the process of catalytic combustion we used dry sediment with the particle size less than 1 mm to provide a stable supplying the sediment through an ejector into the reactor.

The incineration of the sludge was carried out within a test bench setup (Fig. 1). The reactor (1) equipped with an organizing nozzle, was charged with catalyst IR-12-73 (CuMgCr₂O₄/ γ - Al_2O_3) with the size of spherical particles equal to 1.5-2.0 mm, in the amounts of 400 cm³. The reactor was 40 mm in diameter, the height being 1000 mm. With the help of an external electric heater (3), the catalyst layer in the reactor was heated up to a desired operating temperature value ranging within 500-700 °C. Then, through the rotameters (4) was supplied air under a gas distribution grid for the fluidization of the catalyst bed, and to an ejector (7). The total air feeding rate was equal to $3 \text{ m}^3/\text{h}$. Solid waste in the amount of 360 g/h was fed from a

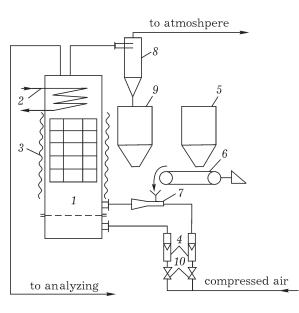


Fig. 1. Schematic diagram of the bench installation for the catalytic combustion of solid waste: 1 - reactor, 2 - heat exchanger, 3 - external heater, 4 - rotameters, 5 - hopper for solid fuel or waste, 6 - transporter, 7 - ejector, 8 - cyclone, 9 - reservoir for collecting ash, 10 - control valves.

hopper (5) by means of a conveyor (6) to an ejector (1), further the waste together with air was supplied to the bottom of the catalyst fluidized bed. The excess heat released in the course of combustion of solid wastes was output with the help of a water-cooled heat exchanger (2). Solid combustion waste products were separated from the effluent gases in a cyclone (8) and were collected in a container (9).

The composition of gaseous products was determined by the method of chromatography using LHM-80 chromatograph with a thermal conductivity detector. As the carrier gas we used helium. The separation of CO, CH₄, H₂, O₂, N₂ was performed using a column with NaX. A Poropac Q column was used for the separation of CO₂, SO₂ and O₂ + N₂. The content of nitrogen oxides in the effluent gases was determined photocolorimetrically with the Griess-Ilosvay reagent by means of the standard method described in [7].

The content of moisture, volatile matter and ash in the initial sediment and solid combustion products were determined by means of technical analysis according to the State Standards GOST 11014-2001, GOST 6382-2001, GOST 11022-95, respectively.

TABLE	1
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Composition of the mineral part of wastewater
sediments (according to X-ray fluorescence analysis)

Mass fraction, %	Elements
10-50	Fe, Si, Zn
1.0-10	Al, Ca, K
0.1-1.0	Zr, Y, Sr, Rb, Cu, Ni, Cr, Mn, Ti, S
<<0.1	Pb, Hg, Cl, P

The elemental composition of the organic part of sediments was determined by means of standard methods described in [7].

A semi-quantitative analysis of the mineral component of the sediment was carried out by means of X-ray spectral method on a VRA-20 apparatus with a fluorescence analyzer. The mercury content was determined using data resulting from X-ray fluorescence analysis with the use of repeated multiplication.

The N_2 adsorption and desorption isotherms for the samples were registered using a Micromeritics ASAP 2400 analyzer.

RESULTS AND DISCUSSION

At the Novosibirsk Gorvodocanal Co. the waste water sediments (WWD) after primary and secondary sedimentation basins were dehydrated to obtain the moisture content of 70-80 mass % by centrifugation, being before the burial were kept for a long time in sludge fields. According to technical analysis data, the dry solid residue from sludge fields contains 62.5 % of minerals. In the mineral part of the sediment, there were more than 20 different elements revealed (Table 1). The main elements are presented by Fe, Si, and Zn. Such elements as Al, Ca, and K are

TABLE 2

Elemental composition of the organic part of the wastewater sediment

Sample	Mass fraction, %							
No.	С	Η	Ν	Р	Cl	S	0	Σ
1	18.2	2.5	1.9	0.4	0.2	0.8	13.5	37.5
2	36.0	4.8	2.3	-	-	0.6	16.4	60.1

Note. Sample 1 – sediment from the sludge fields, Sample 2 – sediment after centrifugation.

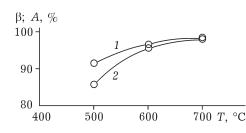


Fig. 2. Changing the burnout level of the sediment β (1) and its ash content A (2) depending on the process temperature.

present in greater amounts (several percent). The content of other elements including a wide range of heavy metals as well as sulphur, phosphorus and chlorine, ranges within tenths and hundredths of percent. The organic part of the sediment, including sulphur, chlorine and phosphorus, amounts to 37.5 % (Table 2).

Comparing to the sediment obtained immediately after treatment in a centrifuge, the content of organic component in the sediment from the sludge fields decreases from 60.1 to 37.5 % (see Table. 2). The content of carbon and hydrogen decreases two-fold, whereas the amount of oxygen and nitrogen demonstrate a 1.2-fold decrease. To all appearance, in the course of storing the sediment in the sludge fields, a partial decomposition occurs, as well as the oxidation by atmospheric oxygen with the removal of hydrocarbon components to the atmosphere or groundwater.

Figure 2 demonstrates the change in the burnout level of WWD from the sludge fields depending on the temperature in the catalyst fluidized bed. It is seen that even at 500 °C the burnout level of the sediment is equal to 94 %. With increasing the temperature up to 700 °C the burnout level increases up to 98.2 %. With increasing the temperature, the ash content in solid combustion products increases, too (see Fig. 2).

Porosity analysis data for the initial sediment and for solid WWD combustion products are presented in Table 3. The specific surface area of the initial sample amounts to $2 \text{ m}^2/\text{g}$. At the combustion temperature of 500 °C the surface area of ash residue increases up to $14 \text{ m}^2/\text{g}$. With increasing the combustion temperature, the average pore radius increases and the surface of ash samples decreases.

For the process temperature of 700 °C, the chromatographic analysis of the exhaust gas-

Temperature, °C	Specific surface area, m ² /g	Total pore volume, cm ³ /g	Average pore diameter, Å
120*	2	-	_
500	14	0.032	88
600	11	0.026	99
700	7	0.025	140

TABLE 3

Parameters of the porous structure for initial sediment and solid products of its catalytic combustion

* Initial dried sediment.

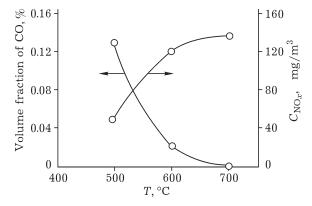


Fig. 3. Changing the concentration of CO and NO_x in effluent gases at different temperature values.

es demonstrated the absence of products of incomplete combustion (CO, CH₄). As the temperature of the combustion process reduced, the concentration of CO in the effluent gas increases to amount up to about 0.22. % at 500 °C (Fig. 3). At the same time, the concentration of NO_x in effluent gases decreases from 131 to 42 mg/m³.

The organic part of the sediment contains sulphur, phosphorus, chlorine. When burning the sludge, a part of these elements is bound with the mineral component of the sediment, the remaining amount such as HCl, SO_x , P_2O_5 enters into the gas phase. In order to determine the concentration of HCl, SO_r , P_2O_5 the effluent gases from the reactor (after the removal of ash in the cyclone and on a porous glass filter) were passed through distilled water. Basing on the analysis of the solution obtained we calculated the concentration of hazardous substances in exhaust gases. At the process temperature value amounting to 700 °C at the reactor outlet the concentration of HCl in gases amounted to 50 mg/m³, whereas that of SO_3 was equal to 130.9 mg/m³ and that of P_2O_5 being of 0.22 mg/m³. Taking into account the data presented in Table 2 and the content of Cl, P and S in the effluent smoke fumes outgoing from the reactor one could conclude that the best binding with the mineral part is observed for P_2O_5 (Table 4): the binding level for this product is as high as 99.98 %. The level binding with the mineral part for HCl is equal to 77.2 % that for SO_3 is equal to 93.3 %.

Most hazardous are mercury and its compounds, since even at 400 °C the mercury compounds (sulphates, chlorides, and oxides) decompose with the formation of elemental mercury. The mercury content in the original dry

TABLE 4

Maximum permissible emission level and concentration values for substances entering into the gas phase at the sediment combustion temperature of 700 $^{\circ}\mathrm{C}$

Parameters	Hg	HCl	\mathbf{SO}_3	P_2O_5	CO	NO_x
MPE, g/s	$2.33\cdot 10^{-3}$	1.49	7.46	0.37	7.46	0.63
RE, g/s	$1.08\cdot 10^{-3}$	0.14	0.36	$0.5\cdot 10^{-3}$	-	0.30
$C_{ m e/g},~ m mg/m^3$	0.46	59	154	0.22	-	131
$\alpha_{ab},~\%$	44.6	77.2	93.3	99.98	-	_

Notes. 1. MPE is the maximum permissible emission at the height of 15 m and the gas temperature of 120 °C for the setup capacity of 1 t/h with respect to dry solid sediment. 2. RE is the real emission levels calculated for the setup productivity of 1 t/h with respect to dry solid sediment based on experimental data. 3. $C_{e/g}$ is concentration of pollutants in the effluent gases produced by the combustion of wastewater sediments in the laboratory setup. 4. α_{ab} is the binding level for toxic substances with respect to the mineral part of wastewater sediment.

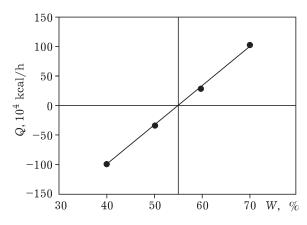


Fig. 4. Quantity of heat (Q) for the catalytic combustion of wastewater sediments in the autothermal mode depending on the sediment moisture content (W).

sediment was equal to 7 mg/kg, whereas that in the ash residue after the catalytic combustion of the sludge at 700 °C amounted to 5 mg/kg. Thus, only 45 % of the mercury is bound with the mineral part. Correspondingly, the concentration of mercury in the effluent gases is equal to 0.45 mg/m^3 .

Table 4 demonstrates data obtained from the calculation of the maximum permissible emission level for toxic substances in the course of combusting 1 t/h of dry WWD from the sludge fields at 700 °C. The real emission of toxic substances from the effluent gases is to a considerable extent lower than their maximum permissible emission level.

The operating mass of WWD taken from sludge fields possesses the following composition, %: C 5.48, H 0.76, O 4.02, N 0.57, Cl 0.06, P 0.12, S 0.23; ash 18.76, moisture 70. The calorific value for the sediment is equal to 112 kcal/kg. Because of the low calorific value for the WWD incineration process at 700 °C, it is necessary to introduce additional fuel; amount of additional heat required for the process depending on the moisture content in the sediment is presented in Fig. 4. The calculation of the setup operating parameters for different values of moisture content in the wastewater sediments indicate that the autothermal operation mode could be achieved when the moisture content in the sediment is equal to 54 %. When heating the air supplied to the fluidized catalyst bed there is a possibility for performing the combustion of the sediment in the autothermal mode at the expense of effluent gases heated up to 700 °C, *i. e.* without supplying additional fuel source or drying the initial sediment.

Catalysts used in the fluidized bed are made with special demands: 1) high catalytic activity, sufficient to provide beginning the combustion process at the lowest possible temperature, 2) the stable activity after prolonged (3–4 thousand hours) operation under the conditions of minimum excess air and of the temperature of the fluidized layer up to 700 °C, 3) resistance against mechanical abrasion (the wear level no more than 0.5 % a day), 4) resistance with respect to catalyst poisons. At the present time, the pilot units and pilot plants with a fluidized bed use catalysts based on transition metal oxides those satisfy the above mentioned requirements.

CONCLUSION

Thus, the catalytic incineration of wastewater sediments from sludge fields allows one to disburden the sludge fields from accumulated sludge and to improve the environmental situation around urban waste disposal plants. With using the heat of effluent gases, the combustion could be carried out in autothermal mode with no additional costs for purifying the effluent gases from hazardous substances those are present among the traditional combustion products.

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