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Energy potential of hazardous waste: key environmental problems of its recovery

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Abstract. *The report is devoted to the problem of processing hazardous carbonaceous waste containing chlorine and heavy metals, based on the "Waste-to-Energy" approach. Plasma energy sources are used to improve the reliability and safety of processing technologies. The most general assessments of the energy efficiency of plasma-steam gasification processes are made and their environmental advantages are shown. The role of the formation of nitrogen oxides in such technologies is also studied.*

Keywords: *hazardous waste, sewage sludge, gasification, vitrification, plasma technologies.*

Environmental risks, including potential pollution of air and soil, remain a major obstacle to utilizing the energy potential of waste in processing technologies. The most dangerous are dioxins and furans formed in the incineration processes of waste containing chlorine. In addition to chlorine-containing waste, for which processing methods are relatively well established, sewage sludge represents a more challenging category of hazardous waste to manage. Their formation is largely associated with previous periods of society's development, when many environmental problems were postponed to a later period. In the 70s and 80s, in many cities, wastewater from electroplating and radio-technical industries was discharged into the sewers in the absence of local treatment. Therefore, a complex challenge arises in localizing the heavy metals – hazardous toxicants – contained within their composition.

The logic of developing hazardous waste processing technologies is, on the one hand, to carry it out in modes close to gasification, and on the other hand, to organize this process in such a way that the hazardous components of the waste are converted into a state in which they are neutral in relation to the environment. If the principle of "Waste-to-Energy" is also followed and, for example, excess electrical energy is produced over one's own needs, the process can become commercially attractive. As we have shown earlier on the basis of a detailed thermodynamic analysis [1], the most effective is the combination in the processing process of both the additional energy of the plasma generator and the thermal energy obtained as a result of partial combustion of waste in an oxygen environment. This gasification mode is non-stoichiometric. The first of them ensures the reliability and safety of the gasification process of generally substandard fuel, which is waste. However, the main source of thermal energy input into the process should be the chemical energy of carbon. Using the example of plasma gasification of sewage sludge, the composition of which can be represented by the gross formula $CH_{2.5}O_{0.5}$, such a gasification regime can be described by a thermochemical equation of the following form [1]:

$$CH_{2,5}O_{0,5} + KH_2O + LO_2 \rightarrow CO + MH_2 + ECO_2 + DH_2O + Q_{TR,} \quad (1)$$

where $Q_{TR} = Q_R + \Delta Q$ is the total thermal energy, one of the components Q_R of which is released as a result of chemical reactions in a mixture of a given composition, and the other ΔQ is introduced into the gasifier by a plasma jet in such a way as to achieve the required temperature T_R for obtaining gasification products. In this form, the gasification process using plasma-steam technologies is most acceptable for analytical consideration.

The solution to the problem of heavy metals is based on the so-called vitrification of the ash residue in the gasification process in the liquid slag removal mode. In this case, heavy metals remain incorporated in the lava-like mass of this melt after its cooling, and therefore lose the ability to leach into the environment. (The slag granules after cooling have a glassy appearance, hence the name of the process – “vitrification”). Its implementation requires a temperature level of over 1400 °C, which is easily achievable using plasma technologies.

The feasibility of using gasification technologies for the processing of hazardous carbon-containing waste has been substantiated by us repeatedly (see, for example, [2]). Indeed, the gasification processes of hazardous chlorine-containing waste are characterized by a long (more than 2 s) stay of product gases in the region of high temperatures (more than 1100 ºC). It is necessary for the chemical decomposition of dioxins and furans, which are formed in the region of intermediate, relatively low temperatures characteristic of combustion processes. On the other hand, this mode is convenient for conducting gasification processes of such waste, as a result of which, in addition to the actual utilization of the waste itself, a valuable chemical or energy resource is simultaneously obtained - a mixture of $CO + H_2$, which is known as synthesis gas. In such a process, almost all components in the reactor region (with the exception of a small amount of nitrogen oxides [3]) reach an equilibrium mode. This allows us to almost unconditionally use the assumption of thermodynamic equilibrium.

The advantage of the gasification process in a non-stoichiometric mode is the ability to introduce additional thermal energy into the process due to partial combustion of the raw material to compensate, for example, significant energy costs for liquid slag removal and vitrification of the ash residue, taking into account that the ash content of the sewage sludge can be as high as 60%. Quantitative estimates for such a process within certain limits regarding excess oxygen blowing were determined in [1]. Its limiting indicator is zero efficiency, when all oxygen is consumed for complete combustion of the raw material, and therefore, instead of gas synthesis, a non-combustible mixture of $CO_2 + H_2O$ is obtained, i.e. the installation switches to the incinerator (waste incineration device) operating mode.

The key requirement for waste processing technologies, as already noted, is the absence of atmospheric air pollution instead of pollution of the earth's surface. In this regard, the role of nitrogen oxides NOx, the appearance of which is characteristic of high-temperature processes [4], may be of fundamental importance for the application of plasma technologies. A feature of taking into account the effects associated with the formation of nitrogen oxides NOx is the fundamental impossibility of using the assumption of thermodynamic equilibrium conditions of the process, as is done in relation to other components of the gasification process (see, for example, [3]). Moreover, in the conditions of plasma processes, the use of simplified models for assessing the role of NOx, such as "fast oxides", is unacceptable. The fact is that they are valid only in the region of relatively low temperatures characteristic of combustion processes, and not plasma [4].

Therefore, the results of our previous studies [5], based on rigorous kinetic calculations, are used here. Despite the fact that these results are obtained in a numerical calculation, they are characteristic of all hazardous waste gasifiers using plasma-air technologies, since such gasifiers must meet standard requirements for temperatures in the working volume of the gasifier and the residence time of product gases in them. The elementary volume of air, entering the plasmatron, moves quite quickly in it, and then relatively slowly in the gasifier. This reflects the logarithmic time scale on the abscissa axis in Fig. 1. Two mixtures are analyzed here: dry air $N_2/O_2 = 3.72 / 1$ and moist air $N_2/O_2/H_2O = 3.72 / 1 / 0.112$. Nitrogen oxide NO, formed at high temperatures, shown in the left part of Fig. 1,a decomposes rather slowly when the air is cooled, as can be seen from Fig. 1,b. This is due to the fact that the rate of its formation-disintegration reaction drops sharply with decreasing temperature - this is the so-called "quenching" effect.

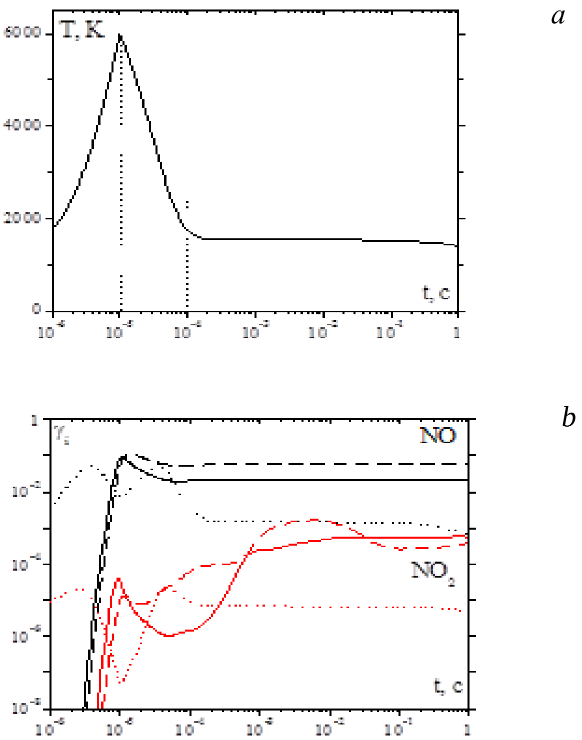

Fig. 1. Character of change in temperature of local air volume during movement in plasmatron and reactor (a) and concentration of NO and NO_2 in them (b): solid and dashed lines – results of chemical non-equilibrium calculation, dotted line – results of equilibrium calculation.

From these calculations it follows that in the plasmatron jet a deviation from the equilibrium value of the NO concentration begins to be observed, and the NO_2 concentration retains its equilibrium value; further, in the reactor itself, NO continues to remain in a non-equilibrium state, and NO_2 also becomes non-equilibrium, but retains its equilibrium value at the current temperature in relation to the aforementioned non-equilibrium value of NO, with which they are strongly related based on the reaction

$$NO + O_2 = NO_2 + O. \qquad (2)$$

As a result, the concentrations of NO and NO_2 exceed the equilibrium values by one and a half to two orders of magnitude for the local temperature at the reactor outlet.

The formation of NOx requires energy costs, which can be determined based on the plasma-air gasification reaction of sewage sludge, taking into account their formation [5]:

$$\begin{gathered} \mathrm{CH_{2,5}O_{0,5}} + K\mathrm{H_2O} + (L+\Delta)\mathrm{O_2} + 3{,}76(L+\Delta)\mathrm{N_2} \rightarrow \mathrm{CO} + \\ +M\mathrm{H_2} + c_{\mathrm{NO}}\mathrm{NO} + c_{\mathrm{NO2}}\mathrm{NO_2} + [3{,}76(L+\Delta) - (\Delta - 0{,}5c_{\mathrm{NO2}})]\,\mathrm{N_2} - Q_{\mathrm{TR.}} \end{gathered} \tag{3}$$

Here are introduced numerical coefficients characterizing both the nitrogen content in the air and the content of nitrogen oxide and dioxide in the gasification products $c_{NO} = 6.35 \cdot 10^{-2}$ and $c_{NO2} = 3.55 \cdot 10^{-5}$ according to [5], and their total indicator $\Delta = 0.5c_{NO} + c_{NO2}$.

It can be shown that the additional increase in energy costs for the formation of NOx is almost 5%.

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