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# Thermodynamic Analysis of the Processes of Plasma Treatment of Low-Level Radioactive Waste in Shaft Furnaces

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**Abstract**—The thermodynamic aspects of the process of plasma treatment of radioactive waste in shaft furnaces were considered. Thermodynamic simulation of the formation of pyrogas during plasma treatment of waste was carried using the example of "Piroliz" and "Pluton" pilot-commercial facilities for solid radioactive waste treatment. It was shown that the thermodynamic simulation method allows fairly adequately describing the changes in the composition of the pyrogas withdrawn from the shaft furnace at different waste treatment regimes. This offers a possibility of developing environmentally and economically viable technologies and small-sized low-cost facilities for plasma treatment of radioactive waste to be applied at currently operating nuclear power plants.

**Keywords**: plasma processing, low-level radioactive waste, shaft furnaces, pyrogas, thermodynamic simulation

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The most common technology for radioactive waste treatment, which allows significantly reducing the waste volume, is waste incineration in furnaces. In this technology, only combustible waste components isolated by sorting are sent for incineration. A drawback suffered by the technology of direct incineration of radioactive waste consists in formation of ash with concentrated radioactive isotopes, dangerous for transportation, dusty, and unsuitable for burial [1].

The use of furnaces for heating and chambers for afterburning off-gases from liquid or gaseous hydrocarbon fuel incinerated in excess air leads to large volumes of flue gases that need treatment for removing radioactive and harmful chemical substances prior to release into the atmosphere. For example, the efficiency of grate combustion of organic components of waste is provided by two- or threefold excess of the air supplied.

These shortcomings are not characteristic for the technology of pyrolysis of solid low- and medium-level radioactive waste with the use of plasma heating sources, electric-arc plasma torches. This technology reduces the waste volume up to 80 times compared to the initial volume; it yields a devitrified slag exhibiting high mechanical strength and chemical resistance, suitable for transportation and long-term burial. Furthermore, by contrast to traditional technology of

**Table 1.** Radioactive waste treated on "Pluton" facility [8]

| Waste component | Content, wt % | Waste component | Content, wt % |
|---|---|---|---|
| Paper | 10–90 | Debris | 4–25 |
| Wood | 2–50 | Thermal insulation materials | 5–25 |
| Textiles (rags) | 2–25 | Metal scrap | 1–10 |
| Plastics (polyethylene, etc.) | 2–25 | Ion exchange resins | 0.3–5 |
| Glass | 2–25 | Deposits | 2–25 |
| Rubber | 2–5 | Vegetable materials with soil | 2–20 |
| Chlorinated polymers | 2–5 | Total ash content of waste | 10–50 |
| Electric boards, electronic components | 2–15 | Total moisture content of waste | 5–40 |

**Table 2.** Parameters of the technology for solid radioactive waste treatment on "Pluton" and "Piroliz" facilities [7]

| Parameter | "Piroliz" | "Pluton" |
|---|---|---|
| Facility type | Counter shaft furnace with melter | |
| Capacity, kg $h^{-1}$ | 40–50 | 200–250 |
| Specific consumption of electric power for treatment, kWh (waste kg)$^{-1}$ | 1–2 | 0.4–0.6 |
| Shaft and melter warm-up time, h | 8–12 | 16–24 |
| Plasma torch type | Indirect-heating electric-arc plasma torch | |
| Number of plasma torches | 1 | 2 |
| Plasma-forming gas | Air | |
| Temperature of the gases leaving the shaft, °C | up to 550 | 200–300 |
| Melter temperature, °C | up to 1550 | 1200–1500 |
| Off-gas afterburner chamber heater | Plasma torch | |

thermal treatment involving formation of flue gases containing harmful inorganic and organic substances, the concentration of highly toxic polychlorinated dibenzo-*p*-dioxins and dibenzofurans (in toxic equivalent terms) in the pyrogas leaving the plasma shaft furnace is substantially lower than that in the flue gases leaving the waste incineration furnace [1].

Further development of plasma technologies for radioactive waste treatment is limited by high degrees of escaping of volatile radionuclides (tens of percent), primarily of cesium-137, from high-temperature units of plasma facilities. Effective optimization of these technologies can only be based on comprehensive analysis of the processes occurring during interaction of the waste with plasma. Here, we will focus primarily on the thermodynamic aspects of the process of plasma treatment of radioactive waste.

The development and optimization of plasma waste treatment technologies extensively uses computer simulation of both physicochemical processes and the dynamics of the gas stream in plasma furnace [2–6]. The processes that occur during heating of waste with complex composition, e.g., radioactive waste, and during their interaction with the hot plasma-forming gas stream are not sufficiently understood. Therefore, models of plasma treatment of solid waste comprise a large number of experimentally determined parameters which depend substantially on the waste type, composition, and morphology, as well as on the shaft furnace geometry. Furthermore, simultaneous modeling of chemical processes and dynamics of the gas stream and solid particle motion requires large computing power and, consequently, fairly long time. Certainly, such calculations are not acceptable in situations where prompt decision-making is essential, e.g., in the case of automated or semi-automated control of the plasma treatment process. Thus, development of effective methods suitable for fast and precise simulation of plasma treatment of waste is of special importance.

Plasma treatment of waste is conducted mostly in shaft furnaces. Examples of such furnaces can be found in "Piroliz" and "Pluton" pilot-commercial facilities developed by Radon Research and Production Association, State Unitary Enterprise, for solid radioactive waste treatment [7]. A typical shaft furnace for solid waste treatment includes a waste loading device, a shaft where the waste is dried and prepyrolyzed, and a melter with plasma torches mounted on the roof for heating the waste to high temperatures (not below 1500°C). In the melter the

**Table 3.** Composition of the model radioactive waste treated on "Piroliz" facility [9–11]

| Waste component | Content of component, wt % | |
|---|---|---|
| | waste with high polyethylene content | waste with high ion exchange resin content |
| Polyethylene | up to 46 | – |
| KA-11[a] ion exchange resin (Dowex HCR-S analog) | – | 64% (55 wt % moisture content) |
| Paper | up to 44 in total[a] | 12 |
| Rags | | 12 |
| Soil (loam) | up to 10[b] | 6 |
| Inorganic fluxes | – | 6 |

[a] Indirect data. [b] Sulfonated styrene–divinylbenzene copolymer.

waste is finally converted to a molten slag consisting predominantly of molten nonvolatile oxides of elements contained in the waste.

In simulation of this process, we will presume that the time period between formation of pyrogas at a sufficiently high temperature (above 1500°C) and its leaving the shaft furnace after passing through the shaft will be sufficient for the gas phase composition to approach the thermodynamically equilibrium composition.

Let us consider the possibility of thermodynamic simulation of the formation of pyrogas during plasma waste treatment by the example of the "Piroliz" and "Pluton" facilities (see Tables 1–4).

According to the facility developers' data [9–11], the organic components of the radioactive waste are pyrolyzed in a shaft furnace under oxygen deficiency, while slag melting is performed in an oxidizing atmosphere, so that the organic components of the slag are completely destructed and a more homogeneous product is obtained. However, Table 5 shows that the pyrogas withdrawn from the facilities contains a significant amount of oxygen, which puts in doubt the claimed deficiency of oxidant in the shaft.

Further, let us analyze in more detail the experimental data (see Table 5) on the composition of the pyrogas leaving the shaft furnace in the case of treatment of waste with high content of polyethylene. A high oxygen content (>5 vol %), along with the presence of hydrogen (9.4 vol %) in the pyrogas withdrawn at a temperature near 500°C, indicates that a significant amount of air entering the shaft furnace through the waste loading device is mixed with the pyrogas leaving the melter. Similarly to the channel by which the pyrogas is removed from the furnace, this device occurs in the top part of the shaft. Under presumption that the air entering through the loading device has virtually no time to react with the pyrogas components, the composition of the pyrogas leaving the melter can be evaluated (Table 6).

**Table 4.** Parameters of the technology of treatment of radioactive waste with high polyethylene content and waste with high ion exchange resin content on "Piroliz" facility [9–11]

| Parameter | Value |
|---|---|
| Diesel fuel consumption, kg $h^{-1}$ | up to 3 |
| Electric power input (power consumption for treatment, kWh $(waste\ kg)^{-1}$) | 32–45 (2–3.5) |
| Capacity for radioactive waste, kg $h^{-1}$ | 11–15[a] (up to 25) |

[a] Indirect data.

From the waste composition data it will be possible to estimate the amount of the chemical elements in the gasified part of the waste loaded into the shaft furnace (Table 7).

Knowing the chemical composition of the entering waste, it is possible to determine the thermodynamically equilibrium composition of the pyrogas at different temperatures (see figure). The equilibrium composition of the gas phase was calculated with the use of Chemical Workbench 4.0 software package (Kintech Lab, Russia).

This program enables calculations for various models of chemical reactors, including the thermodynamic equilibrium reactor model. The latter model can be used for calculation of the chemical equilibrium of multicomponent heterogeneous systems. This thermodynamic system is considered to be self-contained and closed. A state of thermodynamic equilibrium is achieved in this system via chemical and phase transformations. Also, it is presumed that the system is heterogeneous, consisting of several uniform phases. For this reason the gas components form a separate gas phase, and the condensed substances can be regarded as separate phases of solutions. The thermodynamically equilib-

**Table 5.** Composition of the dried pyrogas withdrawn from the "Piroliz" facility shaft at treatment of model radioactive waste and from the "Pluton" facility shaft at treatment of low-level radioactive waste [4, 9–11]

| Pyrogas component | Treatment of waste with high polyethylene content on "Piroliz" facility | Treatment of waste with high ion exchange resin content on "Piroliz" facility | Waste treatment on "Pluton" facility |
|---|---|---|---|
| CO | 12.2 vol % | 3–12 vol % | 8–20 vol % |
| $CO_2$ | 4.3 vol % | 4–6 vol % | 2–5 vol % |
| Gaseous hydrocarbons | [b] | 0–0.3 vo l% (1500 mg $m^{-3}$) | 5000–56000 mg $m^{-3}$ |
| $O_2$ | 5.3[a] vol % | [b] | 3–7 vol % |
| $H_2$ | 9.4 vol % | 2–7 vol % | 8–15 vol % |
| $N_2$ | 68.8 vol % | 74.7–81.0 vol % | [b] |
| HCl | 26 mg $m^{-3}$ | 100 mg $m^{-3}$ | [b] |
| $SO_x$ | 50 mg $m^{-3}$ | 10000 mg $m^{-3}$ | [b] |
| $NO_x$ | 110 mg $m^{-3}$ | 60 mg $m^{-3}$ | [b] |
| $H_2S$ | [b] | 300 mg $m^{-3}$ | [b] |
| HCN | [b] | 250 mg $m^{-3}$ | [b] |
| Solid aerosol particles | [b] | [b] | 2000–8000 mg $m^{-3}$ |
| Pyrolysis resins | [b] | [b] | 2000–25000 mg $m^{-3}$ |

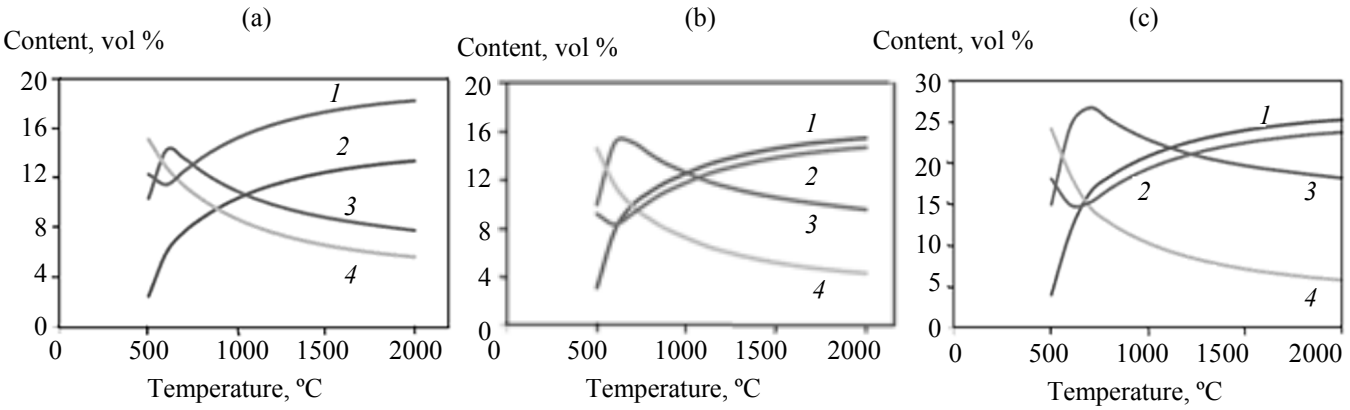
[a] According to [17–19], because of batch loading. [b] Data are not given in the publications.

**Table 6.** Averaged composition (excluding water vapor) of the pyrogas coming from the melter to the top part of the shaft at treatment of radioactive waste on "Piroliz" and "Pluton" facilities

| Pyrogas component | Content of component, vol % | | |
|---|---|---|---|
| | Treatment of waste with high polyethylene content on "Piroliz" facility | Treatment of waste with high ion exchange resin[a] content on "Piroliz" facility | Waste treatment on "Pluton" facility |
| CO | 16.3 | 15.7 | 29.8 |
| $CO_2$ | 5.7 | 7.9 | 7.5 |
| $H_2$ | 12.5 | 9.2 | 22.4 |
| $N_2$ | 65.5 | 67.3 | 40.4 |

[a] The oxygen content in the pyrogas withdrawn from the shaft furnace at treatment of waste with high ion exchange resin content is assumed to be equal to that in the pyrogas withdrawn from the shaft furnace at treatment of waste with high polyethylene content. This assumption is based on the fact that, in these cases, identical amounts of air enter through the loading device with the waste at identical plant capacities.

rium reactor model code uses the main principle of entropy maximum for calculation of the chemical and phase composition. According to this principle, the equilibrium state is characterized by uniform distribution of thermodynamic parameters in the system volume and by the chemical composition corresponding to the maximum probable distribution of energetic levels for macro particles. The program is used for




Equilibrium composition of the pyrogas withdrawn from shaft furnace at treatment on (a, b) "Piroliz" facility of model radioactive waste with high content of (a) ion exchange resins and (b) polyethylene and (c) of radioactive waste on "Pluton" facility in relation to temperature. (*1*) $H_2$, (*2*) CO, (*3*) $H_2O$, and (*4*) $CO_2$.

equilibrium state calculations in cases where external actions on the system can be neglected.

Comparison of the experimentally determined composition of the pyrogas, adjusted for the amount of air entering through the loading device, with the calculated composition showed that the composition of the pyrogas withdrawn from the furnace at a temperature near 550°C correlates, with the relative error not exceeding 10%, with the equilibrium composition of

**Table 7.** Amounts of chemical elements in the gasified part of the waste loaded to the shaft furnace at treatment of radioactive waste on "Piroliz" and "Pluton" facilities

| Component | Amount entering with the waste, kg $h^{-1}$ | Amount entering with air[a] and diesel fuel, kg $h^{-1}$ | Total | |
|---|---|---|---|---|
| | | | kg $h^{-1}$ | kmol $h^{-1}$ |
| Treatment of waste with high ion exchange resin content on "Piroliz" facility | | | | |
| C | 2.6–3.5 | 2.6 | 5.2–6.1 | 0.43–0.51 |
| H | 0.8–1.0 | 0.4 | 1.2–1.4 | 1.2–1.4 |
| O | 5.8–7.9 | 10.5–12.5 | 16.3–20.4 | 1.0–1.3 |
| N | 0 | 34.3–40.7 | 34.3–40.7 | 2.45–2.9 |
| Treatment of waste with high polyethylene content on "Piroliz" facility | | | | |
| C | 6.1–8.3 | 2.6 | 8.7–10.9 | 0.72–0.91 |
| H | 1.1–1.5 | 0.4 | 1.5–1.9 | 1.5–1.9 |
| O | 2.8–3.8 | 18.4–23.3 | 21.2–27.1 | 1.3–1.7 |
| N | 0 | 60.1–75.9 | 60.1–75.9 | 4.3–5.4 |
| Waste treatment on "Pluton" facility | | | | |
| C | 45.8–53.8 | 0 | 45.8–53.8 | 3.8–4.5 |
| H | 11.1–18.0 | 0 | 11.1–18.0 | 11.1–18.0 |
| O | 58.2–133.2 | 11.9–29.9 | 70.1–163.0 | 4.4–10.2 |
| N | 0 | 39.0–97.4 | 39.0–97.4 | 2.8–7.0 |

[a] Calculated on the basis of the content of the components in the pyrogas (see Table 6).

**Table 8.** Experimental and calculated data on the composition (with water vapor excluded) of the pyrogas in the top part of the shaft at treatment of radioactive waste on "Piroliz" and "Pluton" facilities

| Pyrogas component | Content of component, vol% | | |
|---|---|---|---|
| | Treatment of waste with high ion exchange resin content on "Piroliz" facility | Treatment of waste with high polyethylene content on "Piroliz" facility | Waste treatment on "Pluton" facility |
| CO | 17.8/16.3 | 15.8/15.7 | 29.8/32.7 |
| $CO_2$ | 5.3/5.7 | 7.5/7.9 | 7.5/8.2 |
| H2 | 11.6/12.5 | 10.0/9.2 | 22.4/24.6 |

the gas phase at the temperature of 1600–2000°C corresponding to the gas temperature in the melter (Table 8).

Thus, it can be concluded that, during operation of the shaft furnaces, the pyrogas produced in the melter sufficiently rapidly passes through the shaft and is cooled via heat exchange to a temperature near 550°C. At the same time, this period is insufficient for its composition to change significantly following the change in the temperature of the gas phase and due to interaction with the waste fed through the loading device. This is associated, apparently, with the fact that the bags in which the waste is loaded are warmed fairly slowly when moving through the shaft, which complicates the matter exchange between the waste and the pyrogas.

Similar findings were obtained from treatment of waste with high polyethylene content on the "Piroliz" facility (figure, Table 8) and of waste treatment on the "Pluton" facility (figure, Table 8).

The graphic data on the equilibrium composition of the pyrogas show that treatment of model radioactive waste with high polyethylene content on the "Piroliz" facility most closely resembles that at treatment of low-level waste from nuclear power plants on the "Pluton" facility. The main difference consists in a significantly smaller flow rate of the plasma-forming gas, whereby the amount of the pyrogas and, as a consequence, the load on the gas emission treatment system can be reduced. Despite fairly significant differences in the operating regimes between the "Piroliz" and "Pluton" facilities, the thermodynamic analysis in all the cases allowed calculating the composition of the pyrogas withdrawn from the shaft furnace with satisfactory accuracy.

Comparison of the simulation results for plasma treatment of radioactive waste on the "Piroliz" and "Pluton" facilities with the experimental data suggests that the composition of the pyrogas withdrawn from the furnace shaft is formed mainly in the melter, with the content of the components in the gas being close to the thermodynamic equilibrium composition.

Thus, the thermodynamic simulation method allows fairly adequately describing the changes in the composition of the pyrogas withdrawn from the shaft furnace at different waste treatment regimes. Consequently, the results of thermodynamic calculations can be used for controlling the composition and properties of the pyrogas via changing the process parameters. This, in turn, offers a possibility of developing environmentally and economically viable technologies for plasma treatment of radioactive waste. In particular, the controllability of the composition of the pyrogas, in particular, in real time, will allow developing small-sized low-cost facilities for plasma treatment of radioactive waste, which can be applied at currently operating nuclear power plants.

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