Plasmachemical processing of germanium-containing mineral and technological raw materials

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Abstract. This work is a study of the possibility of plasma-chemical enrichment of fly ash. In experiments with a flow reactor, the recovery rate was more than 99% in slag and 70–80% in unmelted particles. In experiments closed in germanium with the melting of the mineral part of the ash in a reactor with a flowing melt film, an extraction degree of 95–96% was obtained, and the enrichment degree can be estimated as 30–40.

1. Introduction
Germanium refers to scattered metals. Direct extraction of germanium from mineral raw materials, as a rule, is not economically feasible, therefore the extraction of germanium is due to the accompanying products of various kinds of technologies. Currently, the main raw material base for obtaining germanium is the coals of the Novikovsky and Pavlovsky deposits. The primary extraction of germanium from coal is carried out by burning it in layered furnaces and the subsequent capture of fly ash. The germanium content in the resulting fly ash is 0.1–1%. A further increase in the concentration of germanium is produced by the method of reduction-sulfidizing electric melting [1–7]. The method is environmentally hazardous, since it is associated with the use of sulfur and is characterized by large losses of germanium, reaching 10–20%. Therefore, the task of developing environmentally friendly methods for increasing the extraction of germanium during the pyrometallurgical production of germanium concentrates from the products of layer-by-layer burning of coal in boiler houses of the Far East is very urgent. To solve this problem, a plasma-chemical method is proposed for extracting germanium by transferring it to the gas phase in the form of monoxide and separating the mineral part of the ash from it in the form of molten slag. The aim of the work was to study the possibilities of plasma-chemical enrichment of germanium-containing fly ash.

Thermodynamic modeling of the Ge-O-C-N system, performed using the “Terra” (chemical and phase equilibrium simulation software), showed (see Figure 1) that the minimum temperature for the existence of GeO is 900°C. Those, for a given composition of the mixture, monoxide below this temperature is unstable and, depending on the ratio of the components, passes into either Ge (at C >15 g) or GeO₂ (at C <15 g).
2. Experiments with direct flow reactor

In the first experiment, a direct flow plasma-chemical reactor with hot walls was used. The slag was collected in the receiving cup, the waste gases were not captured. Experiments were conducted to investigate the possibility of plasma-chemical extraction of germanium with the following parameters: air consumption – 2 g·s\(^{-1}\), consumption of germanium-containing ash from burning coal – 1.5 g·s\(^{-1}\).

The dependence of the degree of extraction of germanium in the gas phase on the composition of the plasma-forming gas was investigated. The composition of the gas phase in the reactor was changed by feeding propane. Ge recovery was determined by its residual content in the treated ash trapped in the receiving beaker. Experiments have shown that as a result of processing raw materials, two types of solid products are obtained: molten slag and powdered ash. The model installation diagram is shown in figure 2.

Figure 1. The equilibrium composition of the mixture: GeO\(_2\) – 1 g, SiO\(_2\) – 70 g, O\(_2\) – 35 g, N\(_2\) – 115 g, C = 15 g.

Figure 2. Model installation scheme.
In the first experiments, the propane feed was 0.18 g·s$^{-1}$ and 0.15 g·s$^{-1}$, which corresponded to the full binding of oxygen in the air to CO2 and H2O. The residual germanium content in the slag was below the sensitivity limit (0.001%) of the method used. The powdery product of plasma-chemical processing was characterized by a low degree of extraction of ~70–80%, which, apparently, is due to large particle sizes, due to which the necessary temperature was not reached.

The following experiments were carried out with a small supply of propane – 0.025 g·s$^{-1}$ (at that, only 20% of the oxygen supplied to the reactor was bound) and without the supply of propane. With propane consumption $G_p = 0.025$ g·s$^{-1}$, the residual germanium content in the slag was 0.03%, and in the slag obtained in the experiment without propane supply – 0.07%, which is more than two times higher than in the previous case. However, in this case, the degree of extraction exceeds 90%.

3. Experiments with melting of ash

Considering the data obtained, as well as the fractional composition of the feedstock (particle size reached 5 mm), it was concluded that the processing of ash with the melting of its mineral part is expedient. This simplifies the processing scheme due to more simple gas separation from the melt of the mineral part of the ash.

To study the scheme for the extraction of germanium with the melting of ash, the installation shown in figure 3 was created.

![Figure 3. The scheme of the pilot plant.](image)

Experiment was carried out with following parameters:
- Ash consumption (a mixture of VBTs-5 and BT-1 – 4/1 by volume) – 8.5 g·s$^{-1}$ (31 g·h$^{-1}$);
- Air consumption – 12 g·s$^{-1}$ (36 m$^3$·h$^{-1}$);
- The power of the plasma torch – 34 kW;
- The temperature of the walls of the reactor – 1350°C;
• Operating time – 720 s;
• The calculated mass of the treated ash – 6100 g.

The products obtained as a result of processing have the following composition in germanium:

1. The initial mixture – 0.71%.
2. Slag receiver:
   2.1. Not melted ash – 0.059%;
   2.2. The top layer of slag is 0.041%;
   2.3. The middle layer of slag is 0.043%;
   2.4. The bottom layer of slag is 0.032%.
3. The water circulating in the capture system is 0.38 g/liter.
4. Sediment in the trapping system (not washed) – 0.12%.

Total results of experiment:
• The mass of the collected slag was – 4600 g;
• The average Ge content in the slag is 0.039%;
• The mass of unmelted ash from slag collector was – 700 g;
• The mass of sediment in the CBA was – 250 g;
• The degree of Ge extraction was 95%, and the degree of enrichment can be estimated as ~ 20.

Thus, experimental verification of the method of plasma-chemical enrichment of germanium gave good results both in terms of the degree of extraction and in the degree of enrichment.

Plasma-chemical processing of germanium-containing ash in a plasma-chemical reactor with a flowing melt film showed that the degree of extraction of germanium from the ash was 95–96%. The residual germanium content in the slag was 0.04% with the initial content of 0.65%. In the experiments, the supply of propane to the reactor was not used and the residual germanium content in the slag approximately corresponded to the previous experiments in the direct-flow reactor without the supply of propane. Thus, by optimizing the composition of the gas phase in the reactor, it is possible to further increase the degree of germanium extraction from the feedstock. The separation of germanium monoxide from the gas phase was carried out with water using a centrifugal bubble apparatus installed at the exit of the plasma-chemical reactor.

Thus, the experiments carried out showed the possibility of efficient plasma-chemical separation of germanium from low-concentrated raw materials with the degree of enrichment in the resulting product up to 30–40 times.

4. Findings
• Perhaps effective (up to ~96%) extraction of germanium from ash in the atmosphere of air (without the addition of propane) without its preliminary grinding;
• To ensure a higher (~99%) degree of germanium extraction, the design of the reactor must ensure the possibility of supplying liquid or gaseous hydrocarbons;
• In order to obtain a high degree of enrichment (20–30 times), the design of the reactor must ensure the possibility of the deposition of ash and carbon on the surface of the molten slag, as well as the mixing of the resulting melt;
• The CBA provides effective capture of Ge and can be applied in the scheme for obtaining technical GeO2.

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