

N.M. Velikonskaya, N.V. Nikolenko,

Yu.D. Khrutskaya, V.V. Velichko

## **PHYSICAL AND CHEMICAL STUDY OF LEACHING PROCESS OF GERMANIUM FROM ASH WASTE**

*Abstract. The analysis of the content of Ge in ash and slag waste produced by burning power coal. Using thermodynamic simulation programs were determined values of pH and E for the existence of ionic forms of germanium at different temperatures of leaching with hydrochloric and sulfuric acids. Improved the method of spectrophotometric determination of germanium by phenylfluorone. Considered the effect of surfactants on the spectrophotometric characteristics of phenylfluorone germanium.*

*Keywords: fly ash, germanium, leaching, thermodynamic equilibrium, spectrophotometric analysis.*

### **Problem formulation**

The use of secondary raw materials and solution the resource-saving problems lead to necessity of research into alternative sources of metals, the development of technologies for their preparation and processing. To do this, you must carry out a comprehensive analysis of secondary materials, in particular coal and its combustion products - ash and slag waste. Under the ash and slag waste is understand the ash and slag that are forming during the burning coal process. That type of waste is a concentrate of impurity elements (germanium, gallium, scandium, yttrium, tungsten, and molybdenum).

### **The purpose of the article**

Ukraine has about 25 billion tons of industrial waste and their number is increasing by 150 - 200 million tons per year. The share of waste from coal production, coal beneficiation and ash and slag waste accounts for about 22% of the total industrial waste. Using of coal as the valuable mineral is implemented only partially. Really is extracted from coal and ashes just some impurity elements [1]. In addition, an integrated approach to the use of ash and slag waste is relevant in terms of addressing environmental problems.

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From the accurate determination of the chemical composition of the ash and slag waste, metal distribution in the processing of coal, depending the direction of their future use. Recycling of ash and slag waste in an industrial plant can provide from one to several tens of tons of rare and scattered metal per year [2].

The purpose of this study is theoretical justification of opportunities for a obtaining the given product - germanium concentrate from fly ash from power coal burning.

### **Main material**

For the development of technology of germanium extraction from coal and its combustion products is necessary to know the chemical composition and the distribution of germanium depending on the type of coal. Samples of coal from different coal-bearing areas (Lisichansk, Almazno-Marevsk, Seleznev, Krasnodon, Bokovo-Hrustalsk and Dolgano-Rovenetsk regions) were studied by semi-quantitative spectral analysis [1]. Have been allocated a group of elements that concentrate in the coals of certain grades (Table 1,2).

Manganese, vanadium, scandium, molybdenum, yttrium is concentrated in the anthracite. In gas coal - molybdenum, scandium, gallium, and germanium is concentrated in long-flame coal. Germanium content decreases from 11 g/t in the long-flame coal to 2.2 g/t in the anthracite. The average content of impurities that have industrial value in ash more than in the coals. Analysis of the chemical composition of different coals and ash confirms the feasibility of the extraction of germanium from long-flame energy coal, in which the germanium content is 3 times higher than the minimum industrial content.

The study of the phase composition of fly ash from power coal-burning allowsto set the form of germanium in raw materials and macrocomponents to which they are confined. An integrated approach to the study of the phase composition [4] based on the study of the behavior of germanium under the action on a sample of the various reagents in combination with heat, oxidation and reduction. The results of the phase analysis of fly ash from power coal with a chemical composition of Ge - 0,36%, Pb - 1,20%, Al - 6,67%, Si - 23,15%, Fetotal - 3,33%, Zn - 1,02 %, (Ca + Mg) - 8,01%, S - 2,83% were interpreted with using X-ray diffraction studies of these specimens. Germanium is determined by titrimetric and spectrophotometric method. At a temperature of 600 -

650°C germanium passes into the gas phase in the form monoxide (GeO), monosulfide (GeS), and disulfide (GeS<sub>2</sub>). Leaching with 1-5% sulfuric acid at a temperature of 90 - 100°C in a solution of germanium is present as an oxide, dioxide (amorphous modifications and hexagonal) and monosulfide.

Table 1

The average content of trace elements  
in coals of different grades, g/t [1]

Coal grade	Ge	Sc	Ga	Y	V	Be	Mo	Mn
Anthracite	2,2	7,9	11,5	33,9	51	4,5	5,1	660,4
Lean coal (semi-antracite)	3,4	3,9	6,7	17,9	32,4	6,2	2,8	321
Bituminous coal, coking, leaning caking	3,9	4,7	7,1	19	36,6	8,1	2,9	321
Gas	5,9	5,7	44,3	18,1	39,5	7,8	4,1	349,4
Long-flame	11	5,6	8,3	21,4	37,4	19,1	3,5	287

Table 2

Trace elements that reach a minimum industrial content in the coals of various grades

Coal grade	Trace elements, reaches a minimum industrial content	
	In coal	In ash
Anthracite	Y, Bi, Yb, Ti	Mn, Y, Mo, Li, Bi, Yb
Lean coal (semi-antracite)	Y, Be	Li
Bituminous coal, coking, leaning caking	Y, Be	Y, Mo, Mn, Sc, Co, Yb
Gas	Y, Ga, Li, Be, Bi	Ge, Mn, Mo, Sc, Li, Be
Long-flame	Ge, Y, Be, Bi, Yb	Ge, Sc, Ga, Mo, Mn, Co

Conducted the thermodynamic analysis the possibility of water electrolysis reaction, and also leaching with hydrochloric and sulfuric acids. Studied the systems of Ge - water, Ge - sulfuric acid - water (Figure 1), Ge - hydrochloric acid - water (Figure 2) at different temperatures. For this Purba diagrams were built[5]. Purba Diagrams (diagrams of state metal - water) are used to predict the thermodynamic possibility of processes of electrochemical oxidation of metals, the formation of

stable ionic complexes and to solve a number of other issues. Knowing the temperature, pH, and E can be said in what form will be one or another metal upon contact with reagents in aqueous solutions.

For system of germanium - sulfuric acid - water at a temperature of 25°C stable solid phases may be Ge, GeS, GeS<sub>2</sub> and GeO<sub>2</sub>. In the liquid phase anions are present. In this system, germanium decompose water with the evolution of hydrogen (potential value higher than zero), while in the pH range from 0 to 7.8 thermodynamically probable existence of GeO<sub>2</sub> (Figure 1,a). At a temperature of 90° C (Figure 1,b) stable solid phases may be GeS<sub>2</sub> and GeO<sub>2</sub>. In the liquid state - anions. In the pH range from 0 to 7.0 thermodynamically probable existence of GeO<sub>2</sub>.

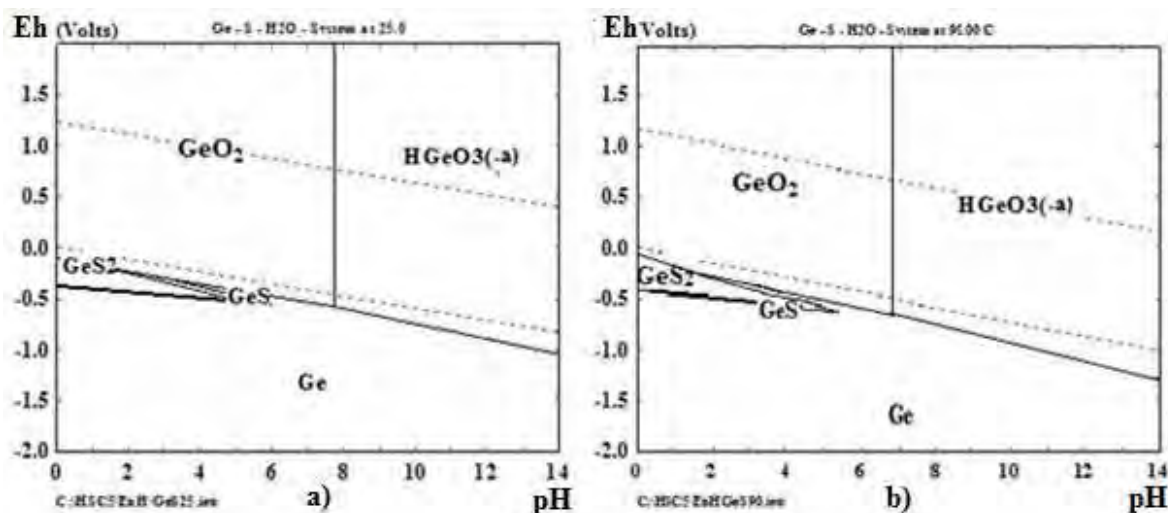
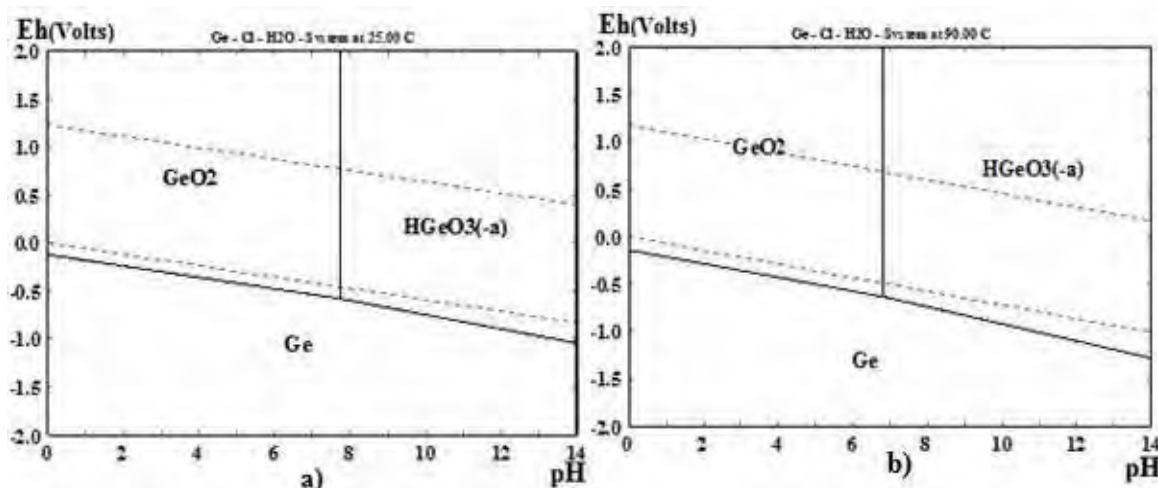


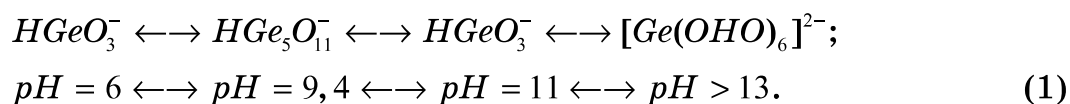
Figure 1 - Diagram E - pH for Ge-H<sub>2</sub>SO<sub>4</sub>-H<sub>2</sub>O system:  
a) T = 25°C, b) T = 90°C

For system of germanium - hydrochloric acid - water at a temperature of 25°C stable solid phases may be Ge, GeO<sub>2</sub>. In the liquid phase anions are present. In this system, germanium decompose water with the evolution of hydrogen (potential value higher than zero), while in the pH range from 0 to 8.0 thermodynamically probable existence of GeO<sub>2</sub> (Figure 2, a). At a temperature of 90°C (Figure 2, b) stable solid phases may be Ge, GeO<sub>2</sub>. In the liquid state - anions. In the pH range from 0 to 6.8 thermodynamically probable existence of GeO<sub>2</sub>.

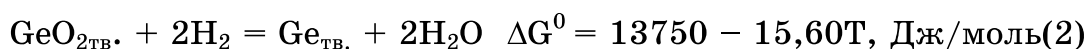
Figure 2 - Diagram E - pH for Ge-HCl-H<sub>2</sub>O system:

a) T = 25°C, b) T = 90°C

Effect of pH on the equilibrium between the various forms of germanate ions [6].



From the resulting after leach solutions is precipitated germanium concentrate. Further reduction of germanium is carried out by gas-reducing agents. The overall reduction reaction and the equation for calculating the Gibbs thermodynamic potential is given in paper [7].



Intensive reduction of germanium dioxide to metallic germanium begins at 600°C, as evidenced by the magnitude of the Gibbs energy, which has a negative value above the specified temperature. Reduction proceeds in two stages with intermediate formation of germanium monoxide:



Figure 3 and Figure 4 shows the calculated values of the changes of Gibbs free energy in the temperature range 900 - 1900 K for the reduction processes of germanium dioxide with gases - CO and H<sub>2</sub>.

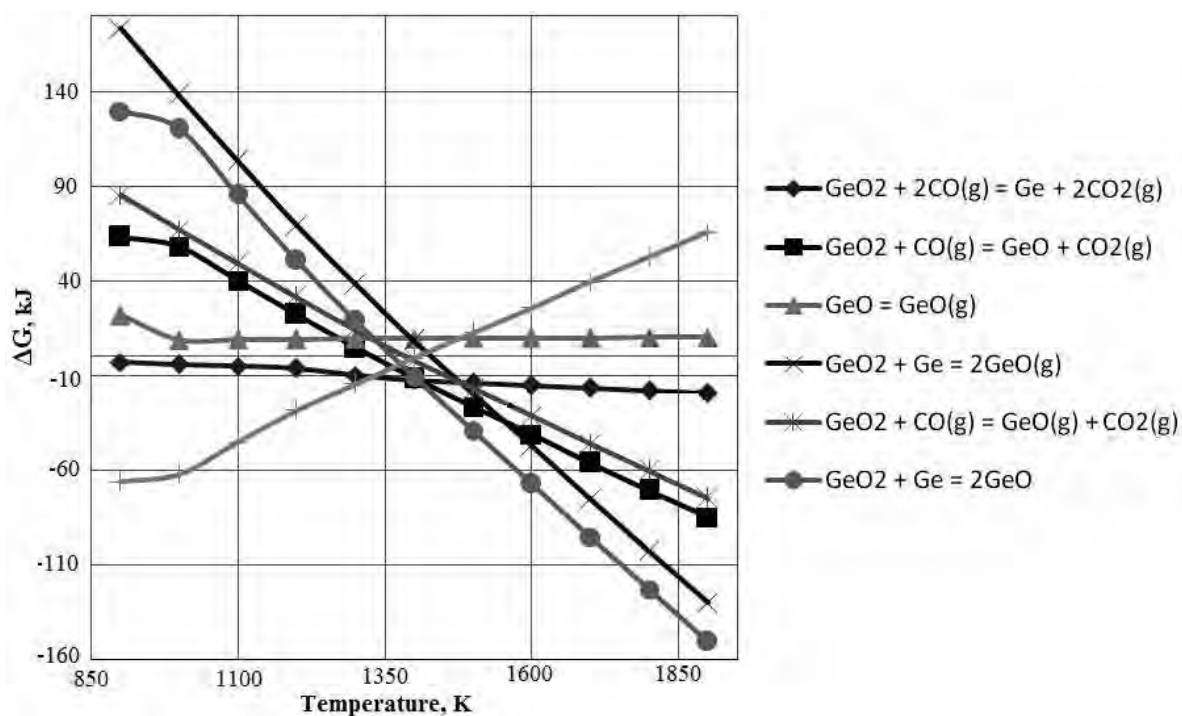


Figure 3 - Change of GeO<sub>2</sub>-CO systems isobaric potential depending on the temperature

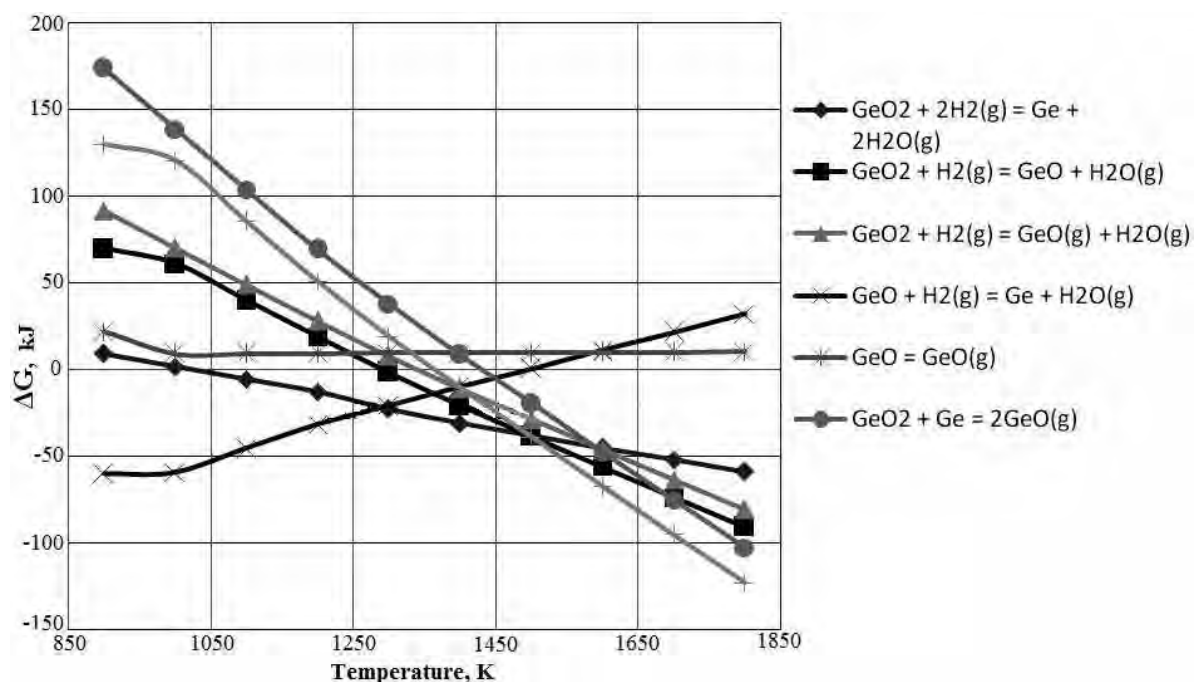
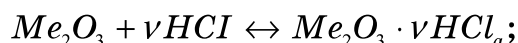


Figure 4 - Change of GeO<sub>2</sub>-H<sub>2</sub> systems isobaric potential depending on the temperature

This method provides the definition of all possible compounds germanium contained in the raw material, regardless of the achieving the equilibrium conditions of reaction (in equilibrium conditions germanium is in the raw materials is in the form of dioxide, germanates, silica-germanate or  $(\text{Si,Ge})\text{O}_2$ ; in nonequilibrium conditions can expect the presence of elemental germanium, its sulfide or monoxide). It can be concluded that the processes occurring in the formation and trapping fumes from coal combustion, provide the lack of nonequilibrium phases of germanium and of dioxide of tetragonal modification in them, the formation of the soluble form of  $\text{GeO}_2$ , and also that the germanium is in easy-open phases of the macro-components. This explains the extraction of germanium from this raw material by conventional methods by acid with high percent of extraction ( $\approx 80\%$ ). To increase the degree of extraction of germanium to 94.64% is proposed [8] to conduct the reduction process at  $P = 1\text{-}10\text{ Pa}$ ,  $T = 1473\text{ K}$ . To date, this method of reduction is in laboratory tests.

We have done the spectrophotometric analysis of germanium content in fly ash and in the original coal. Interaction fly ash with hydrochloric acid is described by equations in stages:



In the first stage there is an equilibrium:



$\text{Me}_2\text{O}_3 + \nu\text{HCl}_a \Leftrightarrow \text{Me}_2\text{O}_3 \cdot \nu\text{H}_3\text{O}^+ + \nu\text{Cl}^-$ , caused by state of acid in solution.

For the opening of of samples and determination of germanium content in the fly ash from the combustion of coal used in the Dnieper TPP, was improved methodology for spectrophotometric analysis. As reagent was used the phenylfluorone, to stabilize complexes and to improve the spectrophotometric characteristics were used various combinations of surfactants of cationic and nonionic type and derivatives thereof. Established the optimum pH, defined molar extinction coefficient and calculated the constant instability of the equation:

$$K_H^1 = \frac{(C_{Ge} - x) \cdot (C_R - 2x)}{x}; x = \frac{A_C}{A_{\max}}, \quad (5)$$

where  $x$  - equilibrium concentration of the complex in solution;  $C_{\text{Ge}}$  and  $C_{\text{R}}$  - total concentration of Ge and reagent in solution respectively;  $A$  - absorption of the solution at a stoichiometric ratio of germanium and trihydroxyfluorones;  $A_{\text{max}}$  - the same with reagent excess.

### Conclusions

1. The chemical and phase analysis of coals and refined products showed that in Ukraine the main source of a germanium is fly ash from power coal burning. Significant germanium content, three times more than the industrial, shows prospects of using ash and slag waste.

2. Considered the thermodynamics of the successive stages of germanium extraction from fly ash by reacting with hydrochloric and sulfuric acids, and also during the reduction of germanium (IV) by reduction gases.

3. Improved the method of spectrophotometric analysis. Established the molar coefficient of light absorbance for the studied combinations germanium - phenylfluorone - surfactant. Determined the boundaries of subordination of the analyzed systems to Beer's law, calculated instability constants of the complexes formed.

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