THERMODYNAMIC INVESTIGATION OF THE BEHAVIOR OF ASH-FORMING COMPONENTS IN BURNING COAL

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A thermodynamic approach to description of the behavior of the fuel–oxidizer system in burning coal is employed to reveal the basic regularities of the process of redistribution of the chemical elements of its mineral part among the ash-forming components. It is shown that the composition of the mineral part is of prime importance in this process.

Burning of coal is a process of chemical interaction between its organic part (organic matter) and an oxidizer. Current models of the organic part of coal consider it as an ensemble of condensed aromatic, hydroaromatic, and heterocyclic structures (clusters) containing different functional groups in the form of substituents [1]. The basis for the organic part of coal is formed by the elements C, H, O, N, and S. The mineral part of coal is presented mainly by the oxides of the elements Ca, Al, Fe, Si, Mg, K, and Na that form the components of ash in the process of high-temperature conversion of the coal.

Interest in the behavior of the ash-forming components in the process of burning of coal has been aroused in connection with the development of new technologies of utilization of coals and, in particular, with the problem of production of combustion products with a high electrical conductivity [2]. At present, investigations of such kind are primarily aimed at solving the issues of environmental protection [3].

The composition of ash and the conditions of its formation have an effect on the behavior of numerous toxic microimpurities in the products of combustion of coal. As has been shown in [4], in its oxygen gasification, a major portion of volatile sulfur can combine with the ash components, which is a powerful means of reducing the discharge of sulfur compounds to the atmosphere. Polychlorinated dioxins are formed on the surface of volatile-sulfur particles in the region of temperatures of 600–700 K [5]. Different compounds based on Cu, Fe, Al, and Si which are present in the ash act as the catalysts of the chlorination reactions. Ash components are involved in the process of chemical binding of heavy metals [6], whose emission to the environment has recently caused the greatest environmental damage [7]. Among the processes decreasing the toxicity of the combustion products of coal are also physical adsorption of volatile mercury compounds by the particles of ash [8].

The emission of light-ash particles to the atmosphere stimulates a number of atmospheric chemical processes. In particular, Fe and Mn compounds are catalysts in oxidation of SO_2 on solid aerosol particles and in cloud droplets [9], while Ca, Na, K, and Fe compounds are involved in conversion of toxic chromium compounds [10].

Among the theoretical methods of investigation of the behavior of the ash-forming components of coal in the high-temperature region, of greatest interest is a thermodynamic analysis. Despite some limitations associated with the impossibility of taking into account the kinetic features of the process, a thermodynamic calculation of the composition and thermophysical properties of the combustion products of coal, under different conditions of the process (temperature, pressure, element composition of the coal, excess-oxygen coefficient, and others), is the only computational method of investigation of a complex, multicomponent, multiphase chemically reacting system represented by the products of combustion of coal.

Numerous works are devoted to a thermodynamic investigation of the composition of the combustion products of coal. In one recent work ([11]), the calculation was carried out for high-ash and low-ash coals with a high content of Si and Al in the mineral part. In the present work, an analogous calculation has been carried out for the coals of

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two main coal basins of Russia — the Kuznetsk Basin and the Kansk-Achinsk Basin, which differ strongly from each other.

1. The mineral part of a solid fuel consists of a large number of different mineral substances the main of which are [12] aluminosilicates (clay (argillaceous) substances, for example, kaolinite $Al_2O_3.2SiO_2.2H_2O$), silica SiO_2 (main component of sand), carbonates ($CaCO_3$, $MgCO_3$ and $FeCO_3$), sulfides (FeS_2 and CaS), sulfates ($CaSO_4$, $MgSO_4$, and $FeSO_4$), iron oxides (FeO, Fe_3O_4, and Fe_2O_3), and salts of alkaline metals (chlorides and sulfates). In most cases, aluminosilicates, carbonates, and sulfides taken together account for up to 95–98% of the mineral part of a solid fuel. Coals also contain 0.01 to 0.5% of chlorine [13], which volatilizes in burning and can be responsible for the hazardous corrosion of heat-exchanger surfaces.

By their origin, the mineral substances forming part of a solid fuel are subdivided into the internal substances accumulated in the strata of the fuel in the process of its formation and partly related to its organic matter and the external substances that find themselves in the fuel in the process of its mining. Whereas the content of the former is more or less constant for a given field, the amount of the latter is prone to variations and strongly depends on the method of mining the fuel. Direct determination of the composition of the mineral part of a fuel involves great difficulties in view of the complexity of its structure. Therefore, in analytical practice, it is conventional to judge the content of mineral substances in coal from the amount of ash left upon combustion of a coal sample in free access of air.

Ash is the product of full or partial oxidation of the mineral components of a fuel. In combustion, the organic matter of the fuel is transformed to CO_2 and H_2O while the mineral substances undergo a number of complex chemical transformations which are due, in most cases, to a change in the mass. In particular, in heating above 1150 K, carbonates are totally decomposed with the release of CO_2:
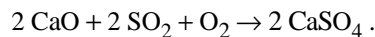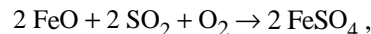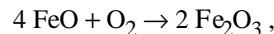
$$CaCO_3 \rightarrow CaO + CO_2 \;;$$
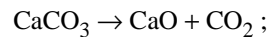
pyrite heated in the case of excess air burns up
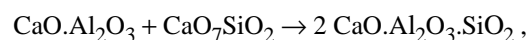
$$4\,FeS_2 + 11\,O_2 \rightarrow 2\,Fe_2O_3 + 8\,SO_2 \;;$$
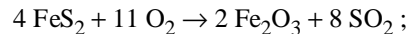
clay substances, silicates, and gypsum lose crystallization water

$$Al_2O_3.2\,SiO_2.2\,H_2O \rightarrow Al_2O_3.2\,SiO_2 + 2\,H_2O \,,$$

$$CaSO_4.2\,H_2O \rightarrow CaSO_4 + 2\,H_2O \,.$$
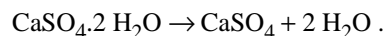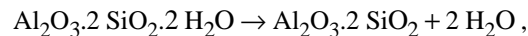
Certain mineral substances partially volatilize (chlorides of alkaline metals). A number of reactions lead to an increase in the mass of the mineral substances:

$$4\,FeO + O_2 \rightarrow 2\,Fe_2O_3 \,,$$

$$2\,FeO + 2\,SO_2 + O_2 \rightarrow 2\,FeSO_4 \,,$$

$$2\,CaO + 2\,SO_2 + O_2 \rightarrow 2\,CaSO_4 \,.$$

An example of a more complex solid-phase chemical reaction occurring in several stages is provided by the process of formation of anorthite ($CaO.Al_2O_3.2SiO_2$) in the ternary system $CaO–Al_2O_3–SiO_2$ at a temperature of 1350–1450 K [15]:

$$m\,CaO + n\,Al_2O_3 \rightarrow m\,CaO.n\,Al_2O_3 \,,$$

$$2\,CaO + SiO_2 \rightarrow 2\,CaO.SiO_2 \,,$$

$$CaO.Al_2O_3 + CaO_7SiO_2 \rightarrow 2\,CaO.Al_2O_3.SiO_2 \,,$$

$$2 \text{ CaO.Al}_2\text{O}_3\text{.SiO}_2 + 2 \text{ SiO}_2 \rightarrow \text{CaO.Al}_2\text{O}_3\text{.2 SiO}_2 + \text{CaO.SiO}_2 \, .$$
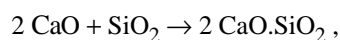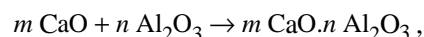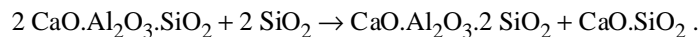
Anorthite forms a continuous series of solid solutions with albite ($\text{Na}_2\text{O.Al}_2\text{O}_3\text{.6SiO}_2$) produced as a result of the chemical interaction between the mineral components in the ternary system Na_2O–Al_2O_3–SiO_2. Another example of the solid-phase chemical reaction occurring at a temperature of 1250–1500 K is the decomposition of kaolinite with the formation of mullite ($3\text{Al}_2\text{O}_3\text{.2SiO}_2$).

As a result of the chemical reactions occurring in the mineral part of coal in its burning, the amount and composition of the ash formed are never identical to the original mineral substances. It has been established that in most cases the ash consists completely, in practice, of Ca, Al, Fe, Si, Mg, K, and Na oxides which are either in the free state or in the form of different compounds [14]. The results of a mineralogical analysis of the light ash of a coal-fired thermal electric-power station [16] show that the main ash-forming components are aluminosilicate glass, mullite, quartz (SiO_2), magnetite (Fe_3O_4), anorthite–albite, anhydride (CaSO_4), hematite (Fe_2O_3), and lime (CaO).

Description of the behavior of a complex, multicomponent, multiphase chemically reacting system (this system is represented by the combustion products of coal) involves great difficulties associated with the necessary of taking into account a large number of heterogeneous chemical reactions, many of which are not understood, in practice. Therefore, of prime importance in understanding the nature of interaction between the components of such a system is the method of thermodynamic analysis that enables one to evaluate the efficiency of the redistribution of chemical elements among the components of the system under conditions of rapid establishment of the state of chemical equilibrium.

2. As is obvious from the results of an analysis of different thermodynamic calculations, the obtained equilibrium composition of the chemically reacting system is very sensitive to the selection of the initial information. In calculation, one must take into account all possible compounds as applied to the system in question. Thermodynamic data on them must be correct and consistent. Considerable disagreement in the final results can also occur when different computational procedures and convergence criteria are employed [17].

In the present work, to find the thermodynamic characteristics of the high-temperature conversion of coal we have employed the TETRAN software system [18] designed for automated calculation of the chemical composition, the thermodynamic properties, and the transfer properties of multiphase systems as applied to the products of combustion or conversion of organic fuels in the range of temperatures of 300–6000 K and in the range of pressures of 10^{-2}–10^2 MPa. Continuous operation of the system showed its reliability, a stable convergence of iteration processes with an insignificant consumption of computer time, and the adequacy of the results obtained to the values observed experimentally. A distinctive feature of the system is direct calculation of heterogeneous chemically reacting systems with no preliminary analysis of the possibility for the condensable substances to appear. The operation of the system is ensured by the Bank of Initial Thermodynamic Data, which contains about 2000 different compounds and includes much of the data from the IVTANTERMO-85 Bank of Thermodynamic Properties of Individual Substances [19], data for a number of substances from the JANAF Handbook [20], and some other data on condensed substances.

For a thermodynamic analysis of the process of conversion of the ash-forming components in burning a solid fuel we have selected TR Kuznetsk coal of underground mining of the Kuznetsk Basin and B2-R Berezovskii coal of the Kansk-Achinsk Basin with a higher-than-average ash content; these grades of coal differ strongly in the composition of the mineral part. We took the following original composition of the Kuznetsk coal per working mass (%): W = 1.8, A = 19.64, C = 70.31, H = 2.99, O = 3.06, S = 0.47, and N = 1.73. The composition of the mineral part was as follows: SiO_2 = 55.4, Al_2O_3 = 25.4, Fe_2O_3 = 7.2, CaO = 4.6, MgO = 1.9, K_2O = 1.9, Na_2O = 0.7, TiO_2 = 1.0, P_2O_5 = 1.6, and MnO = 0.3. For the Berezovskii coal the corresponding composition was equal to (%) W = 12.00, A = 10.56, C = 54.98, H = 3.79, O = 17.90, S = 0.23, and N = 0.54. The composition of the mineral part was SiO_2 = 30.0, Al_2O_3 = 11.0, Fe_2O_3 = 9.0, CaO = 42.0, MgO = 6.0, K_2O = 1.2, and Na_2O = 0.8 [21]. Since an important role in forming the ash matter and redistributing certain compounds among the gas and condensed phases is played by chlorides [11], we added chlorine in an amount of 0.05% of the coal mass to the initial composition of the coals [13].

The calculations were carried out in a two-phase approximation when all the condensed substances are represented in the form of an ideal solution of components which is in equilibrium with an ideal gas. We took account of 275 components, including 123 condensed components. The composition of the condensed phase included simple oxides (SiO_2, Al_2O_3, and others) and oxides containing several elements, sulfates (CaSO_4, $\text{Al}_2(\text{SO}_4)_3$, and others), sul-
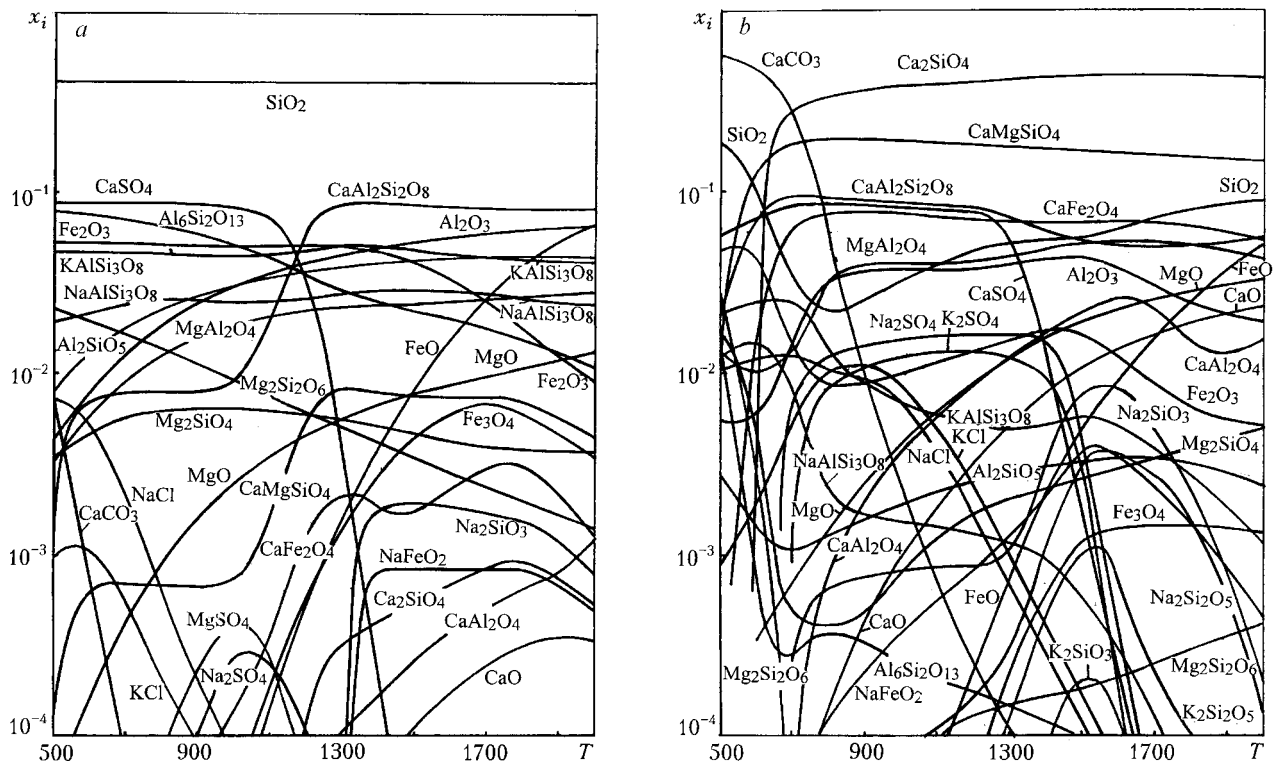
Fig. 1. Equilibrium composition of the condensed phase of the combustion products of Kuznetsk coal (a) and Berezovskii coal (b) (mole fractions x_i) vs. temperature of the process (α = 1.2 and p = 0.1 MPa).

fides (CaS, FeS, and others), chlorides (KCl, NaCl, and others), carbonates ($CaCO_3$, K_2CO_3, and others), nitrates (KNO_3 and $NANO_3$), and hydroxides (KOH, $Ca(OH)_2$, and others).

The oxides containing several chemical elements are of prime importance in the formation of the ash matter. In selecting the initial information for a thermodynamic calculation involving these compounds, on the one hand it is important to prescribe the most complete set of them. It is well known, for example, that 15 chemical compounds — three simple oxides, two ternary compounds ($CaO.Al_2O_3.2SiO_2$ and $2CaO.Al_2O_3.SiO_2$), and 10 binary compounds ($CaO.Al_2O_3$, $2CaO.SiO_2$, $3Al_2O_3.2S\underline{i}$, and others) — are formed in the ternary system $CaO–Al_2O_3–SiO_2$ [15]. The corresponding information for more complex systems can be obtained from different mineralogical sources [22] and based on an analysis of phase diagrams [23].

On the other hand, for the selected set of components we must know their thermodynamic characteristics. The absence of such information for certain compounds significantly impairs the accuracy of the thermohydrodynamic calculation. In the present work, we have employed a rather complete set of thermodynamic data (obtained from [24–28]) for description of the behavior of the oxides containing several chemical elements.

In burning a solid fuel in the combustion chambers of power plants, carbon particles burn in an air atmosphere; the excess-air coefficient α (ratio of the utilized amount of air to its stoichiometric amount for a given coal) is an important operating parameter of the process. Under actual conditions, $\alpha > 1$, i.e., the process of formation of the ash-forming components occurs in an oxidizing medium, although its local values can be less than unity in the course of the process. Therefore, the equilibrium composition of the chemically reacting system coal/air has been calculated for a value of α = 1.2, which is typical of the conditions of direct burning of coal.

3. The results of calculating the equilibrium composition of the condensed phase of the combustion products of Kuznetsk coal in the range of temperature of 500–2000 K at the pressure p = 0.1 MPa are given in Fig. 1a. The mineral part of this coal contains a large amount of silicon and aluminum; therefore, in this case the main ash-forming components are simple oxides SiO_2 (throughout the temperature range) and Al_2O_3 (at a temperature $T > 1500$ K) and mullite ($3Al_2O_3.2SiO_2$) and anorthite ($CaO.Al_2O_3.2SiO_2$) (the latter becomes the main components at $T > 1200$ K). Iron
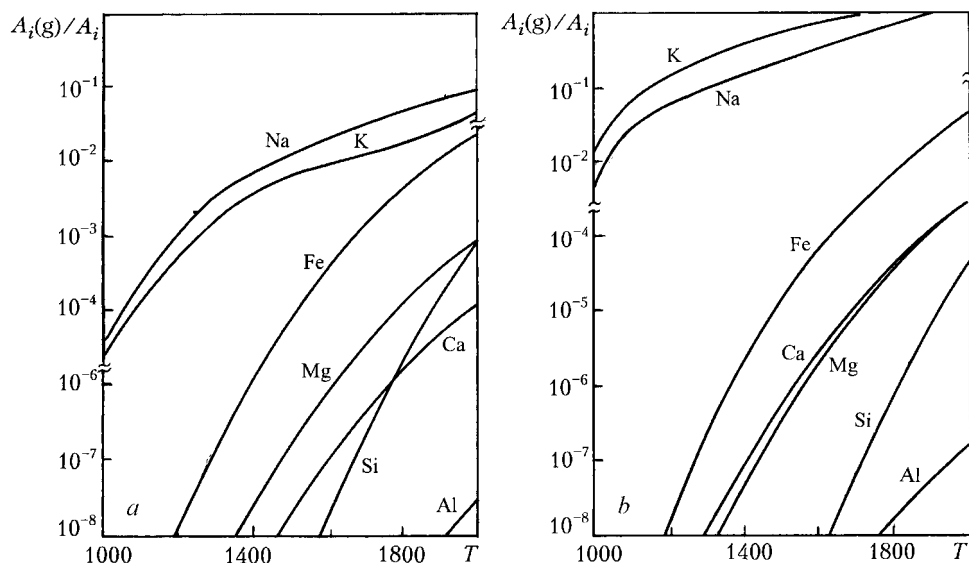
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Fig. 2. Content of different chemical elements A_i in the gas phase of the combustion products of Kuznetsk coal (a) and Berezovskii coal (b) ($\alpha = 1.2$ and $p = 0.1$ MPa).

is presented by the oxide Fe_2O_3, which transforms to FeO when the temperature is higher than 1700 K. At low temperatures, calcium is present in the form of sulfate and it becomes anorthite with increase in the temperature. At low temperatures, magnesium forms part of pyroxene ($2MgO.2SiO_2$), and it becomes magnesium aluminate ($MgO(Al_2O_3)$) with increase in the temperature. Throughout the temperature range, potassium and sodium enter into the ternary compounds $K(AlO_2).3SiO_2$ and $Na(AlO_2).3SiO_2$ in the form of aluminates. Sulfates are presented just by calcium sulfate, while chlorides are presented by a small amount of sodium and potassium chlorides in the region of temperatures lower than 900 K.

A different situation is observed in the condensed phase of the combustion products of Berezovskii coal, the dominant element of whose mineral part is calcium. The results of calculating the equilibrium concentrations of the ash-forming components for this coal (Fig. 1b) show that in the region of temperatures lower than 700 K calcium is presented mainly by carbonate but as the temperature increases it changes to oxides: dicalcium silicate $2CaO.SiO_2$ and monticellite $CaO.MgO.SiO_2$. These oxides also bind the ground mass of silicon and magnesium. Aluminum is presented by anorthite, the magnesium aluminate $Mg(AlO_2)_2$, and the simple oxide Al_2O_3. The ground mass of iron is represented in the form of the dioxide $CaO.Fe_2O_3$, which decomposes with the formation of FeO and CaO at a temperature of the order of 2000 K. In the region of temperatures lower than 1500 K, potassium and sodium are present mainly in the form of sulfates and chlorides. At higher temperatures, the concentration of these elements in the condensed phase sharply decreases, which is attributed to their transition to the gas phase.

Evaluation of the content of these substances in the gas phase is of importance from the viewpoint of the emission of the ash-forming components to the environment. Figure 2 gives calculated data on the concentration of compounds of different elements in the gas phase for the combustion products of the coals in question. It is seen that the tendency toward evaporating strongly depends on the composition of their mineral part. For the Kuznetsk coal the compounds of all the elements are mainly in the condensed phase throughout the temperature range. In the combustion products of the Berezovskii coal, the compounds of potassium and sodium gradually change to the gas phase with increase in the temperature and when $T > 1500$ K the gas-phase components of these elements become dominant. The behavior of the compounds and other elements changes with the composition of the mineral part of coal; therefore, we cannot unambiguously judge the capacity of the compounds of one element or another for evaporating without taking into account the composition of the mineral part of the coal, as has been done, for example, in [11].

NOTATION

W, moisture content of the coal, wt.%; A, ash content of the coal, wt.%; T, temperature, K; p, pressure, Pa; x_i, mole fractions of the components; α, excess-air coefficient.

REFERENCES

1. G. Ya. Gerasimov, *Inzh.-Fiz. Zh.*, **72**, No. 2, 253–259 (1999).
2. I. B. Rozhdestvenskii, G. Ya. Gerasimov, A. G. Gerasimova, et al., in: *Thermodynamic Studies of the Processes of Processing and Burning of Coals* [in Russian], Moscow (1984), pp. 82–96.
3. L. D. Smoot (ed.), *Fundamentals of Coal Combustion for Clean and Efficient Use*, Amsterdam (1993).
4. G. Ya. Gerasimov and T. M. Bogacheva, *Inzh.-Fiz. Zh.*, **74**, No. 3, 193–197 (2001).
5. G. Ya. Gerasimov, *Fiz. Goreniya Vzryva*, **37**, No. 2, 29–34 (2001).
6. D. Verhulst, A. Buekens, P. J. Spencer, and G. Eriksson, *Environ. Sci. Technol.*, **30**, No. 1, 50–56 (1996).
7. H. Van Malderen, S. Hoornaert, and R. Van Grieken, *Environ. Sci. Technol.*, **30**, No. 2, 489–498 (1996).
8. D. Karatza, A. Lancia, and D. Musmarra, *Environ. Sci. Technol.*, **32**, No. 24, 3999–4004 (1998).
9. S. N. Pandis and J. H. Seinfelf, *J. Geophys. Res.*, **D94**, 1105–1126 (1989).
10. C. Seigneur and E. Constantinou, *Environ. Sci. Technol.*, **29**, No. 1, 222–231 (1995).
11. R. Yan, D. Gauthier, G. Flamant, and J. M. Badie, *Fuel*, **78**, No. 15, 1817–1829 (1999).
12. B. S. Belosel'skii and V. K. Solyakov, *Power-Generating Fuel* [in Russian], Moscow (1980).
13. *Valuable and Toxic Elements in Industrial Coals of Russia: Handbook* [in Russian], Moscow (1996).
14. D. D. Ruschev, *Chemistry of Solid Fuel* [in Russian], Leningrad (1976).
15. A. A. Pashchenko, A. A. Myasnikov, E. A. Myasnikova, et al., *Physical Chemistry of Silicates* [in Russian], Moscow (1986).
16. X. Querol, D. V. Fernandez-Turiel, and A. Lopez-Soler, *Mineralog. Mag.*, **58**, No. 1, 119–127 (1994).
17. W. R. Smith and R. W. Missen, *Chemical Reaction Equilibrium Analysis: Theory and Algorithms*, Wiley–Interscience, New York (1982).
18. G. Ya. Gerasimov, N. A. Zhegul'skaya, I. B. Rozhdestvenskii, et al., *Mat. Model.*, **10**, No. 8, 3–16 (1998).
19. L. V. Gurvich, *Vestn. Akad. Nauk SSSR*, No. 3, 54–65 (1983).
20. *JANAF Thermochemical Tables*, 2nd edn., NBS-37, Washington (1971); Suppl. (1974, 1975, 1978, 1982).
21. V. S. Vdovchenko, M. I. Martynova, N. V. Novitskii, and G. D. Yushina, *Power-Generating Fuel of the USSR* (*Fossil Coals*, *Combustible Shales*, *Peat*, *Black Oil*, *and Combustible Natural Gas*): *Handbook* [in Russian], Moscow (1991).
22. L. G. Berry, B. Masson, and R. V. Dietrich, *Mineralogy: Concepts*, *Descriptions*, *Determinations*, San Francisco (1983).
23. F. V. Christyakov (ed.), *Minerals. Handbook: Diagrams of Phase Equilibria* [in Russian], Issue 2, Moscow (1974).
24. F. E. Spencer, J. C. Hendrie, and D. Bienstock, in: *Proc. 6th Int. Conf. on Magnetohydrodynamic Electrical Power Generation*, Vol. 2, Washington (1975), pp. 181–218.
25. J. L. Haas, G. R. Robinson, and B. S. Hemingway, *J. Phys. Chem.*, *Ref. Data*, **10**, No. 3, 575–669 (1981).
26. G. B. Naumov, B. N. Ryzhenko, and I. L. Khodakovskii, *Handbook of Thermodynamic Quantities* [in Russian], Moscow (1971).
27. L. P. Ruzinov and B. S. Gulyanitskii, *Equilibrium Transformations of Metallurgical Reactions* [in Russian], Moscow (1975).
28. V. A. Ryabin, M. A. Ostroumov, and T. F. Svit, *Thermodynamic Properties of Substances* [in Russian], Leningrad (1977).