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THERMODYNAMIC ANALYSIS OF THE BEHAVIOR OF MICROIMPURITIES OF TOXIC METALS IN COAL COMBUSTION PRODUCTS

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The thermodynamic approach to the description of the fuel–oxidizer system is used to elucidate the basic laws of behavior of compounds of the most toxic elements-microimpurities in combustion products of coal (Hg, Pb, Cr, Mn, Ni, Co, and As). It has been shown that the distribution of elements over components of the gas and condensed phases strongly depends on the process temperature and the composition of the mineral part of the coal.

The volume of organic fuels currently used in heat-power engineering causes considerable environmental pollution by combustion products containing, besides the basic components (water vapors and carbon dioxides), a large amount of other substances. Despite their small concentration in combustion products, some of them have a strong negative impact on the biosphere and cause a great amount of material damage.

The complex approach to the problem of environmental pollution by the emissions of power plants also calls for a strict control over the content in combustion products of high-toxicity microimpurities, among which are, in particular, heavy metals. The concentration of heavy metals in carbon varies over a wide range depending on the coal field and considerably exceeds the mean concentrations of these elements in the Earth's crust. According to the USEPA data, among the most toxic elements, whose compounds upon emission into the environment are subject to control, are: As, Be, Co, Cr, Hg, Ni, Mn, Pb, Sb, and Se.

Coal combustion comprises a combination of a large number of complex physicochemical processes involving practically all elements of the periodic system. Among the theoretical methods of investigation of such chemical reacting systems, of greatest interest is the method of thermodynamic analysis. Despite the many limitations connected with the impossibility of taking into account the kinetic features of the behavior of chemical components, the thermodynamic calculation of the composition and thermophysical properties of coal combustion products under different conditions of the process (temperature, pressure, elemental composition of coal, oxidizer excess coefficient, etc.) is practically the only computing method for investigating a complex multicomponent multiphase chemically reacting system, which coal combustion products represent.

The thermodynamic investigation of the distribution of microimpurities of toxic metals over components in coal combustion products has been the subject of many works (see, e.g., [1, 2]). As the analysis of the results obtained shows, this distribution strongly depends on the initial composition of the mineral part of coal. In the present paper, an analogous investigation has been carried out for two main coal basins of Russia — the Kuznetsk and Kansk-Achinsk basins.

1. In estimating the damage caused to the environment by the emission of toxic substances into the atmospheric air, it is customary to use the value of the reduced mass of their total annual release $M = \sum_i A_i m_i$ [3]. The relative aggressiveness index of the ith substance A_i is measured in arbitrary tons per ton of fuel and is defined by the formula $A_i = \alpha_i \delta_i a_i$ (for carbon oxide $a_i = 1$ is taken). In a number of cases, two additional factors are introduced into this formula: correction for the probability of repeated ejection of a given substance into the atmosphere upon its deposition on the surfaces (for dust) and correction for the probability of the formation of secondary substances more dangerous than the initial ones (e.g., for light hydrocarbons).

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TABLE 1. Ecological Characteristics of Elements-Microimpurities of the Mineral Part of Coal

Element	a_i	c_i, mg/kg	$\mathrm{MPS}_{\mathrm{da}}$, mg/m^3
Mercury	4472	0.2	0.0003
Lead	4472	20	0.0003
Chromium	2000	30	0.0015
Manganese	1414	200	0.0010
Nickel	1095	20	0.0010
Cobalt	346	10	0.0010
Arsenic	316	10	0.0030

For toxic metals and their oxides (As, Ag, Cd, Co, Cr, Hg, Mn, Ni, Pb, Pt, Sb, Sn, U, V, Zn), the correction $\alpha_i = 5$. For other metals and their oxides (Al, Ba, Be, Bi, Ca, Fe, Mg, Mo, K, Na, Si, Sr, W) as well as for other components of solid aerosols and for polycyclic aromatic hydrocarbons, $\alpha_i = 2$. For all the other dangerous substances released into the atmosphere, $\alpha = 1$. The correction δ_i for toxic and nontoxic metals is, respectively, 1.0 and 1.2 [3].

Table 1 gives the most toxic (in terms of reduced mass) elements-microimpurities of the mineral part of coal, the indices of relative danger to man of their compounds [3], the mean concentrations in coal [4], and daily average maximum permissible concentrations in the atmospheric air of built-up areas [5]. Below, a brief characterization of these elements is given.

Mercury. Mercury compounds are classified with the most toxic and long-lived microimpurities in the atmosphere. The concentration of mercury in the air varies from 1 to 10^3 ng/m^3 depending on the place of measurement [6]. Natural sources of mercury ingress into the atmosphere include water surfaces, soils, plants, forest fires, volcanos, etc. The main anthropogenic sources of mercury compounds are industry, heat-power plants, and the incineration of rubbish. In the East European countries (including the European part of Russia), anthropogenic emission of mercury compounds into the atmosphere is mainly due to the operation of coal-burning thermal power plants [7].

Unlike the majority of metals constituting small impurities in solid fuel, mercury is an extremely volatile element. Therefore, its compounds are present in combustion products of solid fuel before their release into the atmosphere practically completely in the gaseous phase. The dominant forms of mercury in combustion products are vapors of metal mercury Hg^0, as well as compounds of bivalent mercury: $\mathrm{HgCl_2(g)}$ and HgO(g, s) [8]. Because of the poor solubility of metal mercury in water, clearing of combustion products from Hg^0 is only possible after its chemical transformation into freely soluble compounds of bivalent mercury.

Lead. Lead compounds are also highly toxic. Lead oxides (PbO and $\mathrm{PbO_2}$) exhibit the property of accumulating in the human body, leading to serious consequences for the health of man. The problem of environmental pollution with these substances arose in connection with the fact that appreciable quantities of them are contained in the combustion products of leaded gasoline [9]. The emission of lead during the movement of an automobile burning such a gasoline depends on the quantity of tetraethyl lead $\mathrm{Pb(C_2H_5)_4}$ added to the fuel, which is a very effective and widely used antiknock compound in internal combustion engines.

Lead is a highly volatile toxic metal. As will be shown below, in the combustion zone the compounds of this element practically completely go to the gas phase. The mean concentration of lead in the mineral part of coal is two orders of magnitude higher than the corresponding value for mercury. Therefore, even in the case of using systems for clearing combustion products from ash the emission of this element into the atmosphere can exceed the emission of mercury.

Chromium. Chromium compounds are present in the atmospheric air in aerosol form with a concentration from 0.01 to 1 μg/m^3, respectively, in rural and urban places [10]. Chromium is classified with elements whose anthropogenic emission into the atmosphere exceeds its amount coming from natural sources. The most stable forms of chromium under atmospheric conditions are Cr(III) and Cr(IV). Of these, only the hexavalent form has been recognized as carcinogenic.

Manganese. Manganese compounds are present in the atmospheric air in the form of Mn(III) and Mn(IV), and only solid $\mathrm{MnO_2}$ particles in cloud drops are the basic oxidizer in the heterogeneous process of transformation of Cr(III) salts into its more toxic hexavalent form [10]. The high concentration of manganese in the mineral part of coal and the rather high value of the relative aggressivity A_i place this element's compounds, as to reduced mass, into the category of the most toxic compounds in coal combustion products.

Nickel, Cobalt, and Arsenic. Compounds of nickel, cobalt, and arsenic are less toxic than the compounds of the above-considered elements. Their concentration in the mineral part of coal is two orders of magnitude lower than the manganese concentration. Therefore, the emission of these compounds into the atmosphere with coal combustion products causes a smaller amount of ecological damage to the environment.

2. For thermodynamic analysis of the behavior of microimpurities of toxic metals in coal combustion products, we chose Kuznetsk TR coal of the Kuznetsk basin underground mining and Beryozovsk B2-R coal of a higher ash content of the Kansk-Achinsk basin, widely differing in the composition of the mineral part. The initial composition of the Kuznetsk coal in terms of the working mass was taken to be as follows (%): $W = 1.8$; $A = 19.64$; C = 70.31; H = 2.99; O = 3.06; S = 0.47; N = 1.73. The composition of the mineral part is as follows: $SiO_2 = 55.4$; $Al_2O_3 = 25.4$; $Fe_2O_3 = 7.2$; CaO = 4.6; MgO = 1.9; $K_2O = 1.9$; $Na_2O = 0.7$; $TiO_2 = 1.0$; $P_2O_5 = 1.6$; MnO = 0.3. For the Beryozovsk coal, the corresponding composition is equal to (%): $W = 12.00$; $A = 10.56$; C = 54.98; H = 3.79; O = 17.90; S = 0.23; N = 0.54. The composition of the mineral part is as follows: $SiO_2 = 30.0$; $Al_2O_3 = 11.0$; $Fe_2O_3 = 9.0$; CaO = 42.0; MgO = 6.0; $K_2O = 1.2$; $Na_2O = 0.8$ [11].

The calculations were made by the TETRAN program complex [12] designed for automatic calculation of the composition, thermodynamic properties, and properties of the transfer of multiphase systems as applied to combustion products or conversion of organic fuels. We chose the two-phase approximation, in which all condensed substances are represented in the form of a perfect solution of components which is in equilibrium with a perfect gas. To describe the behavior of prevailing chemical elements of the coal working mass (C, H, O, S, N, Si, Al, Fe, Ca, Mg, K, Na, Cl), we used the thermodynamic model of [13], which permits estimating the efficiency of the redistribution of these elements among the basic gaseous and ash-forming components of coal combustion products under the conditions of quick establishment of the chemical equilibrium state.

The model was extended [13] by including in it one of the chemical elements forming a microimpurity in the working mass of the coal. In so doing, we added to the set of components of the chemically reacting system compounds containing elements-microimpurities: elementary oxides (PbO, Cr_2O_3, etc.) and oxides containing several elements ($MnO.Al_2O_3$, $2PbO.SiO_2$, etc.), sulfates ($MnSO_4$, $CoSO_4$, etc.), sulfides (NiS, MnS, PbS, etc.), chlorides ($HgCl_2$, $NiCl_2$, etc.), nitrides (CrN, Mn_3N_2, etc.), hybrides (MnN, PbH, etc.), and hydroxides ($Mn(OH)_2$, $Co(OH)_2$, etc.). The thermodynamic characteristics of the components needed for the calculations were taken from the bank of thermodynamic data of the TETRAN program complex [12].

In burning solid fuel in the combustion chambers of power plants, coal particles burn in the air atmosphere, and the air excess coefficient α (the ratio of the used quantity of air to its stoichiometric quantity for a given coal) is an important regime parameter of the process. Under real conditions $\alpha > 1$, i.e., the process of toxic compound formation proceeds in an oxidizing medium, although the local values of α, as the process proceeds, can be less than unity. Therefore, the calculation of the equilibrium composition of the coal–air chemically reacting system was performed for $\alpha = 1.2$, which is typical for the conditions of direct burning of coal.

3. Of the microimpurities of heavy metals, the most volatile element is mercury. As mentioned above, mercury compounds are present in coal combustion products practically completely in the gas phase. Therefore, most of their mass passes through purification systems and is released into the environment. Removal of vapors of metal mercury from combustion is only possible after its chemical transformation into readily water-soluble compounds of bivalent mercury.

The mercury content in power-generating coals varies between 0.05 and 0.5 mg/kg [4]. In the process of fuel combustion, mercury goes to the gas phase in the form of vapors of metal mercury Hg^0. At a mean content of this impurity in the source coal of 0.2 mg/kg, the Hg^0 concentration in combustion products is of the order of 30 $\mu g/nm^3$. The process of further oxidation of Hg^0 is rather complicated and consists of a homogeneous and an inhomogeneous reaction of the gas components containing Hg atoms. As is shown in [14], at high temperatures metal mercury vapors react fairly quickly with HCl, Cl_2, and O_2 and more slowly with NO_2 and practically do not interact with NH_3, N_2O, SO_2, and H_2S. The main channel of Hg^0 transformation in coal combustion products is their interaction with HCl in the presence of O_2 [15]. The global kinetic scheme of this process can be represented in the form

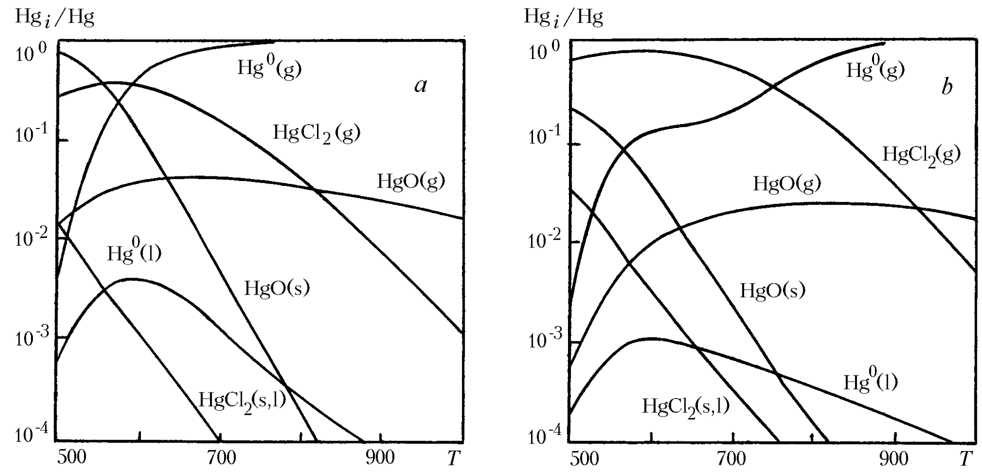

Fig. 1. Mercury distribution among components in combustion products of Kuznetsk coal depending on the process temperature. Chlorine content in the initial fuel: a) 1.0; b) 2.0 g/kg (α = 1.2; p = 0.1 MPa). T, K.

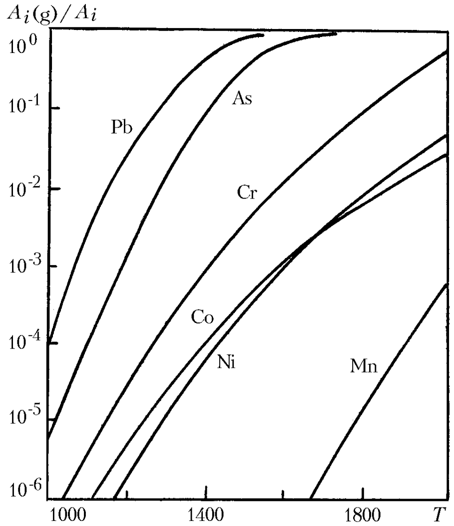

Fig. 2. Content of various chemical elements-microimpurities A_i in the gas phase of Beryozovsk coal combustion products (α = 1.2; p = 0.1 MPa). T, K.

$$2\mathrm{Hg}^0(\mathrm{g}) + 4\mathrm{HCl}(\mathrm{g}) + \mathrm{O}_2 = 2\mathrm{HgCl}_2(\mathrm{s, g}) + 2\mathrm{H}_2\mathrm{O}\ .$$

At low temperatures ($T \le 750$ K) the equilibrium is shifted towards the formation of $HgCl_2$, and at high temperatures $HgCl_2$ reacts with H_2O to form HgO oxide, which subsequently breaks down into Hg^0 and O.

The results of the calculation of the equilibrium distribution of mercury among different components depending on the process temperature for the Kuznetsk coal are given in Fig. 1, where Hg is the total amount of mercury in the system and Hg_i is the amount of mercury in individual elements. The gaseous compounds of mercury are represented by Hg, HgO, and $HgCl_2$. The condensed phase contains HgS, too. Since an important role in the formation of the ash mass and in the redistribution of some compounds between the gaseous and condensed phases is played by chlorides [16], we added chlorine to the initial composition in an amount of up to 2 g/kg.

Analysis of Fig. 1 shows that at high temperatures mercury is practically completely in the form $Hg^0(g)$. As the temperature is lowered, in the oxidizing medium Hg^0 is transformed to the oxide HgO(g), which then reacts with the basic chlorine-containing component HCl to form $HgCl_2(g)$. The HCl concentration is an important parameter of the process. As the chlorine content in the initial fuel is increased to 2 g/kg, the behavior of the concentration curves

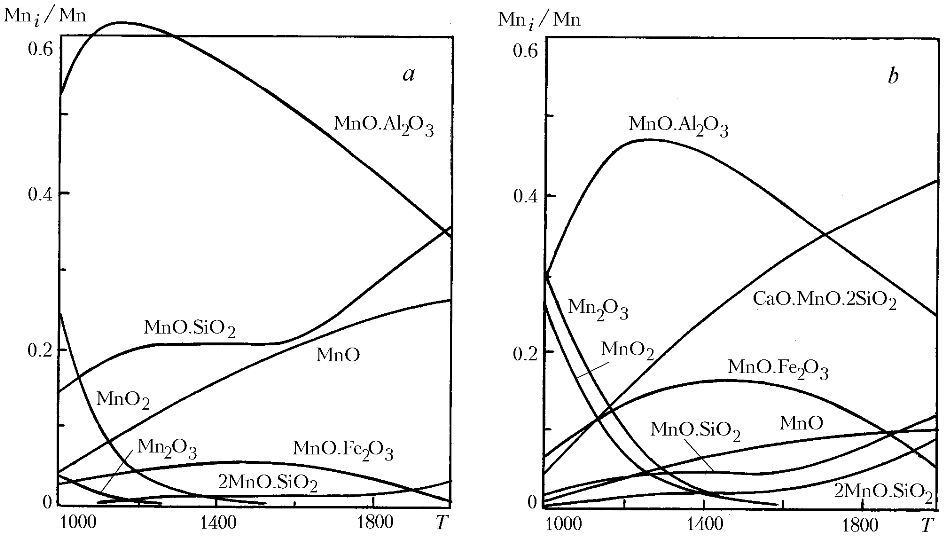

Fig. 3. Temperature dependence of concentrations of the basic condensed components involving Mn in combustion products of Kuznetsk (a) and Beryozovsk (b) coals ($\alpha = 1.2$; $p = 0.1$ MPa). T, K.

sharply changes: the dominant component at temperatures below 750 K becomes chloride $HgCl_2$(g), which is readily soluble in water and can be removed from the gas in systems of wet clearing of combustion products from sulfur oxides. From Fig. 1 it is also seen that an increase in the chlorine content in the gas suppresses the condensation of mercury compounds in the region of low temperatures. A further increase in the chlorine concentration in the system leads to a shift of the point of equality of Hg^0(g) and $HgCl_2$(g) concentrations to the region of higher temperatures and at a chlorine content in the initial fuel of 5 g/kg reaches 900 K, which agrees with the result of the thermodynamic calculation of the composition of combustion products of garbage containing a large amount of chlorine [17].

4. Compounds of other toxic metals are less volatile, and their appreciable content in the gas phase is only observed in the high-temperature range. Figure 2 gives the results of the thermodynamic calculation of the content of various chemical elements-microimpurities in the gas phase of Beryozovsk coal combustion products, which permit estimating the degree of volatility of toxic metals at a given temperature of the process. It is seen that the ability for evaporation increases on going from one element to another in the chain Mn → Ni → CO → As → Pb. The results of the analogous calculation for the Kuznetsk coal give practically the same picture with a 100 K shift of the curves of Fig. 2 towards higher temperatures.

The thermodynamic analysis of the composition of the condensed phase shows that the distribution of elements-microimpurities among the condensed-phase components depends on the process temperature and the composition of the mineral part of the coal. Figure 3 shows the behavior of the concentrations of the basic condensed components with the participation of the least volatile component — manganese — in combustion products of the Kuznetsk and Beryozovsk coals, where Mn is the total content of manganese in the system and Mn_i is the manganese content in individual components. Since the mineral part of Kuznetsk coal contains a large amount of silicon and aluminum, the major portion of manganese is contained in the compounds $MnO.SiO_2$ and $MnO.Al_2O_3$, as well as in the porous oxide MnO, and the role of the first and last compounds thereby increases with increasing temperature. An insignificant portion of manganese is bound by oxides $MnO.Fe_2O_3$ and $2MnO.SiO_2$. At low temperatures the concentrations of oxides MnO_2 and Mn_2O_3 are appreciable.

In the Beryozovsk coal combustion products, whose mineral part contains a large amount of calcium, the main components involving manganese are the complex oxides $CaO.MnO.2SiO_2$ and $MnO.Al_2O_3$. With increasing temperature, the concentration of the first compound becomes dominant. Since the iron content in the mineral part of Beryozovsk coal is higher than in the mineral part of Kuznetsk coal, the concentration of $MnO.Fe_2O_3$ oxide in the condensed phase of Beryozovsk coal is about three times higher than the respective value of Kuznetsk coal. At temperatures below 1000 K, the Mn_2O_3 and MnO_2 oxides become the dominant components.

NOTATION

M, reduced mass of the total annual release into the atmosphere of dangerous substances, tons/year; m_i, mass of annual release of the ith substance into the atmosphere, tons/year; A_i, index of relative aggressiveness of the ith substance; a_i, index of relative danger to man of the presence of the ith substance in the air; c_i, mean concentration of an element-microimpurity in coal, mg/kg; α_i, correction to a_i for the probability of calculation of a given substance or its derivatives in environmental components and in food chains; δ_i, correction to a_i taking into account the impact on various recipients besides man; W, coal humidity, weight %; A, ash content of coal, weight %; T, temperature, K; p, pressure, Pa; α, air excess coefficient; g, l, and s, gaseous, liquid, and solid components; MPC, maximum permissible concentration. Subscripts: da, daily average.

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