

Thermodynamic analysis of the processes of interaction and formation of nitrogen and sulfur compounds during the combustion of Kansk-Achinsk coals

Vladimir Elsukov* and Svetlana Latushkina

Bratsk State University, 40 Makarenko st., Bratsk, Russia

Abstract. The paper identifies and examines the mechanisms of the interaction of nitrogen and sulfur compounds during the combustion of Kansk-Achinsk coals (KAC). The researches were carried out on the basis of the model of extreme intermediate states (MEIS) developed at The L.A. Melentiev Institute of Energy Systems and presented in a number of publications. The KAC of various deposits characterized by different content of sulfur and mineral components are considered. On the basis of computational experiments, the influence of alkaline elements of the mineral part (Ca, Na, K) on the formation of NO and SO₂ was determined. The temperature interval of the transition of condensed calcium sulfate to sulfur dioxide during the combustion of KAC of various (including new) deposits has been clarified. Based on the modeling of thermodynamic states, the results of industrial tests are considered, in which inversely proportional dependences of NO and SO₂ on the resulting calcium sulfate have been recorded. These dependences can be explained by multidirectional energy flows during the formation of CaSO_{4/c} and NO_x.

1 Introduction

It is known that nitrogen oxides (NO) and sulfur oxides (SO₂) are the main gaseous pollutants during solid fuel combustion. Currently, there is insufficient data on the mechanisms of possible influence of these pollutants. The possibility of the influence of sulfur binding processes on the generation of NO was noted in particular by American specialists [1].

2 The study

The present study was carried out using the thermodynamic model of extreme intermediate states (MEIS), developed at the Institute of Energy Systems SB RAS (Irkutsk), B.M. Kaganovich and collaborators [2,3,4]. In [5], a modification of the model is presented, which includes restrictions on macroscopic kinetics and is written by the authors, in relation to these studies, in the form (for fixed pressure, temperature and initial composition of reagents):

find:

$$\max x_j = F(x^{\text{ext}}), \quad (1)$$

under the conditions:

$$Ax = b, \quad (2)$$

$$D_i(y) = \{x: x \leq y\}, \quad (3)$$

$$G(x) = \sum_j G_j(x)x_j, \quad (4)$$

$$x_r \leq \varphi, \quad r \in R, \quad (5)$$

$$x_j \geq 0, \quad (6)$$

where $x=(x_1, \dots, x_n)^T$ is the vector of the quantities of moles of the components of the reaction mixture; $y=(y_1, \dots, y_b)^T$ is the vector of the number of moles of the initial reagents, $y \subset x$; ext is the index of the equilibrium state corresponding to the extremum of the objective function; $A - m \times n$ is the matrix of the contents of elements in the components of the system; b is the vector of the number of moles of elements; $D_i(y)$ is the region (set) of thermodynamic reachability from y ; $G -$ Gibbs energy; $j \in J^{\text{ext}}$ - is the set of indices of components, the extreme concentration of a set of which must be determined; $R -$ sets of indices of constraints on macroscopic kinetics; φ is a constant.

The objective function (1) represents the desired maximum concentration of the harmful substance that we are interested in. Matrix equation (2) represents the condition for preserving the quantities of moles of elements. Expression (3) defines the domain of thermodynamic reachability. The sign « \leq » inside the curly brackets has a thermodynamic interpretation: $x \leq y$, if it is possible to move from y to x along a continuous trajectory along which the characteristic function (in this case G) does not monotonically increase.

The authors included conditions (5) in the block of MEIS restrictions. Restrictions (5) on the maximum concentrations of individual substances were set taking into account experimental data and (or) the results of thermodynamic calculations at individual stages.

* Corresponding author: elswk@mail.ru

The paper considers the KAC of three deposits, the parameters of which are presented in Table 1.

Table 1. The main parameters of the KAC deposits to be taken under consideration.

Parameter	Kansk-Achinsk coals (KAC) of the following deposits:		
	Irsha-Borodinskoye	Bogotolskoye	Berezovskoye
Q_i^f , kJ/kg	15659	10140	15650
S^f , %	0,18	0,49	0,20
A^f , %	6,00	6,72	4,70
CaO, %	25,80	37,30	60,00
Na ₂ O, %	0,50	0,70	0,80
K ₂ O, %	0,50	0,30	1,20

At the first stage of the research, the influence of various components of the mineral part of fuels on the generation of the pollutants in question (NO_x и SO₂) was considered. It was noted in [6] that the alkali metals contained in the mineral part of coal (Ca, Na, K) can interact during the combustion and (or) with sulfur and nitrogen, changing the concentrations of the above pollutants.

Figure 1-2 shows the results of calculations for (1)-(6) burning of Berezovsky coal in two variants. In these variants, the composition of the vector x varied, including (in the first variant in Fig.1) 137 components formed by 15 chemical elements. In the second variant (Fig. 2), condensed calcium sulfate (Na₂SO_{4/c}) was excluded from vector x . Berezovsky coal was selected for this computational experiment as the richest in the content of alkali metals (Na₂O=0,8% отA^d=4%). In both variants, the equilibrium values of nitrogen compounds (x_j^{eq}) were calculated. The characteristics shown in Fig. 1,2, are close to similar dependences based on the results of thermodynamic calculations of the combustion of the KAC Irsha-Borodinsky deposit in the works [2,4]. It can be seen from Fig. 1,2 that at flare combustion temperatures of KAC (1500K), mainly nitrogen oxide (NO) is formed in the furnaces. In the temperature range 1400-1700K, along with NO, the flue gases contain noticeable concentrations of NO₂, NaNO₂, KNO₂, N₂O, HNO₂. Moreover, the concentrations of NaNO₂ and KNO₂, unlike other nitrogen compounds, are maximum at a temperature of ≈ 1500K. It should be mentioned that in accordance with hygienic standards [7] sodium and potassium nitrites are poisonous and 20 times more dangerous than nitrogen dioxide (NO₂). The maximum permissible concentrations (MPC) in the air of the working area, respectively, are 0.1 and 2 mg/ m³. It follows from the above that when burning KAC, along with various nitrogen oxides (NO_x), it is necessary to control the emissions of NaNO₂ and KNO₂. The exclusion of Na₂SO_{4/c} from the vector x led to an increase in the concentration of NaNO₂ (Fig.2) and a slight decrease in NO₂. Such exclusion of Na₂SO_{4/c} is possible, for example, if all the sulfur of the fuel is bound in CaSO_{4/c} during combustion in the fluidized bed. It should be mentioned that the concentration of calcium in the mixture is three or more times higher than the value required for stoichiometric binding of fuel

sulfur. Fluctuations in the concentrations of sodium and potassium nitrite emissions are also possible with changes in the content of Na and K in fuel, which occurs in practice.

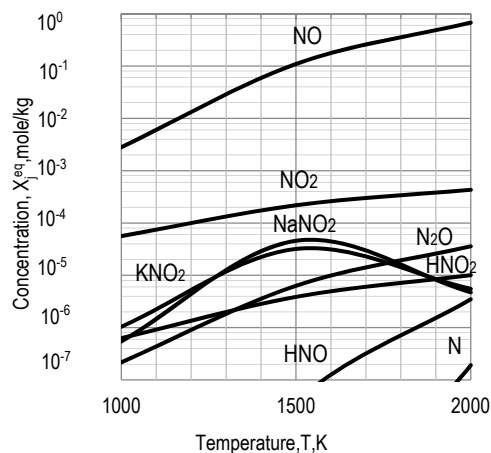


Fig.1. Equilibrium concentrations of nitrogen compounds in the combustion products of the KAC of Berezovsky deposit at $\alpha=1,2$ (with the inclusion of the Na₂SO_{4/c} component in the vector x).

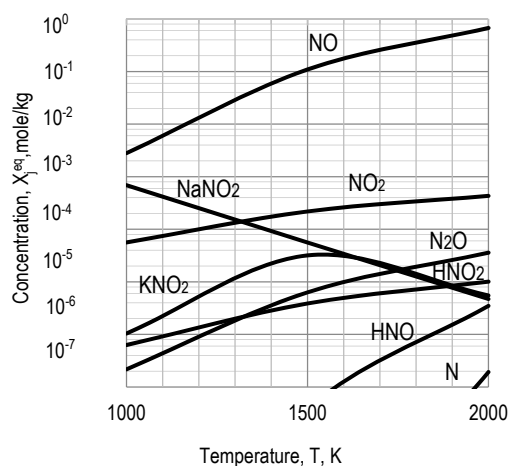


Fig.2. Equilibrium concentrations of nitrogen compounds in the combustion products of the KAC of Berezovsky deposit at $\alpha=1,2$ (without the inclusion of the Na₂SO_{4/c} component in the vector x).

Thus, the amount and type of emissions of nitrogen compounds depend on the conditions of interaction of alkali metals (Ca, Na, K) with both nitrogen oxides and sulfur compounds.

At the second stage of the research, the conditions for the formation of sulfur compounds during the combustion of KAC of the four above-mentioned deposits were considered. The values of temperatures (T) and excess air (α) varied. The results of calculations based on (1)-(6) are presented in Fig.3-4. Fig.3 shows the equilibrium (x^{eq}) values at $\alpha = 1,2$ and temperatures in the range 1000÷1600K. From these figures it can be seen that for all KAC, the temperature interval of transition $x_{CaSO4/c}^{eq}$ in x_{SO2}^{eq} remains approximately constant and is ≈ 1400÷1500K. In the same temperature range, sodium and potassium sulfates are converted into

sulfur dioxide and nitrogen compounds. The values of sulfur in the fuel (vector y) determine the equilibrium concentrations of the components formed $x_{CaSO_4/c}^{eq}$ and $x_{SO_2}^{eq}$, which are greatest during the combustion of the KAC Bogotolskoye deposit. Extreme values $x_{CaSO_4/c}^{eq}$ and $x_{SO_2}^{eq}$ do not depend on temperature and are determined only by the material balance (2).

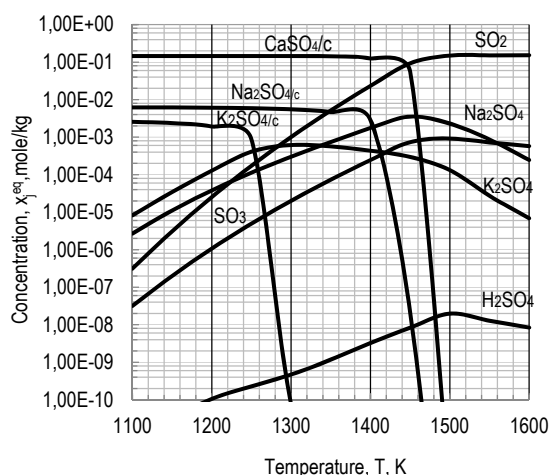


Fig.3. Equilibrium concentrations of sulfur compounds in the combustion products of the KAC of Bogotolskoye deposit ($\alpha=1,2$; $p=0,1$ MPa).

Figure 4 shows the effect of excess air (α) on NO and SO₂ emissions and temperature transitions $x_{CaSO_4/c}^{eq}$ in $x_{SO_2}^{eq}$ for the Irsha-Borodinsky deposit. The calculations were performed at two values of α , respectively 1,1 and 1,2. It can be seen from the figures that at these values of α , the sulfur compounds in question change somewhat only in the temperature range (1400÷1500 K), and outside of it their concentrations are approximately constant (these compounds are only diluted with excess air). Large values of α correspond to large concentrations of CaSO_{4/c} and NO (and at all design temperatures).

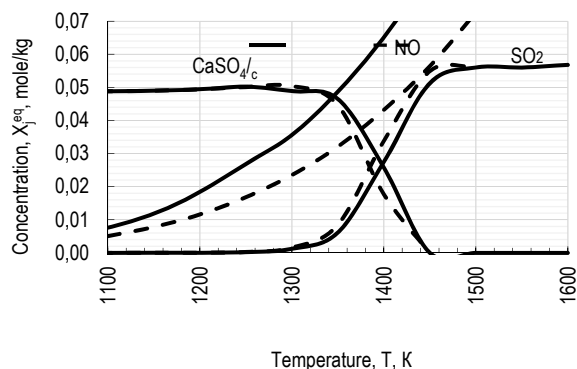


Fig.4. The effect of excess air on emissions NO and SO₂ during the combustion of the Irsha-Borodinsky KAC deposit ($\alpha=1,2$; $\alpha=1,1$).

In the work [8], the authors of the presented study performed an analysis of industrial tests of boilers with

flare combustion of the KAC Irsha-Borodinsky deposit. Conclusions were drawn about the correspondence of experimental data with the calculated temperature range of calcium sulfate formation (1400-1500K) and the influence of α values on its value. The authors explained this by the fact that the time of presence of the combustion products in the region with $T=1400\div1500K$ decreased with the increase of α and the proportion of SO₂ transition to CaSO_{4/c} decreased. By reaction:



Thus, for the considered KAC, the temperature interval of the transition of CaSO_{4/c} to SO₂ is determined by the final equilibrium of the system (combustion products) in accordance with (1)-(6) and is 1400–1500K, and the value of the transition fraction is non-thermodynamic factors (kinetics, diffusion, etc.).

At the last stage of the research, the possibility and conditions of a simultaneous increase in NO concentrations and a decrease in SO₂ were tested at values close to those measured by Japanese specialists in industrial experiments with a fluidized bed [9].

In these experiments, the researchers consistently increased the molar ratio of Ca/S (0; 2 and 4) in the layer at a sulfur content of $S^d = 0.62\%$ and recorded a simultaneous increase in NO_x from about 30 to 75 ppm and a decrease in SO₂ from 140 to 17 ppm. The obtained dependencies are not explained by the researchers.

The authors of the presented work suggested that such dependences can be explained by the multidirectional energy flows of the reactions of the formation of CaSO_{4/c} and NO. From (7) it can be seen that when a mole of CaSO_{4/c} is formed, 500KJ is released, and for NO, on the contrary, 90KJ is absorbed. It is clear that with an increase in the [9] molar ratio of Ca/S, a decrease in the concentration of SO₂ will lead to the formation of CaSO_{4/c} and, accordingly, the release of energy necessary for the generation of NO. To verify this assumption, the authors modeled the conditions of the above experiments in relation to the KAC of the Bogotolskoye deposit (closest to [9]). The objectives of the simulation are to determine the enthalpies (their changes) of the system during the above experiments. Na₂SO_{4/c} was chosen as the target function (1), since the conditions of its formation are close to CaSO_{4/c} (as can be seen from Fig.3,4), but its effect on the concentrations of other sulfur-containing components is insignificant (due to the small content of Na).

The concentration of NO was set from experiments [9] taking into account the conversion of NO_x to NO ($NO=0.13 \cdot NO_x$) by the formula (5) in the form:

$$x_{NO}=\psi, \quad (8)$$

where ψ is the number of moles of NO, which increased sequentially in three calculated experiments (0; 2; 4) (states). The numbering coincides with the mole relations of Ca/S in [9] (for convenience of comparison).

The concentration of SO₂ was also set from experiments [9] by the formula (5) in the form:

$$x_{SO_2}=\varphi, \quad (9)$$

where φ is the number of moles of SO₂, which was consistently reduced in computational experiments in accordance with [9].

Table 2. The results of modeling the combustion process of the Bogotolskoye deposit under thermodynamic and kinetic constraints (T=1073K, $\alpha = 1,2$).

Parameters of the mixture	State of the system						
	y	$x_{Na_2SO_4/c}^{ext}$					x^{eq}
	State numbers						
	1	0	2	4	3	5	6
	Type of restrictions						
	(1)-(6), (8), (9) at			(1)-(4), (6)	(1)-(6), (8), (9) at	(2)-(4), (6)	
	$\psi=0,00082$ $\varphi=29,3$	$\psi=0,0012$; $\varphi=0,0115$	$\psi=0,0024$ $\varphi=0,0036$	$\psi=0$; $\varphi=0$	$\psi=0,0016$; $\varphi=0,0115$		
	Gibbs energy, enthalpy, kJ/kg; concentrations, mole/kg						
G(x)	$-8,506 \cdot 10^3$	$-9,107 \cdot 10^3$	$-1,126 \cdot 10^4$	$-9,102 \cdot 10^3$	$-1,156 \cdot 10^4$	$-9,103 \cdot 10^3$	$-1,662 \cdot 10^4$
H(x)	$2,279 \cdot 10^2$	$-2,053 \cdot 10^2$	$-2,166 \cdot 10^3$	$-2,078 \cdot 10^2$	$-2,425 \cdot 10^3$	$-2,078 \cdot 10^2$	$-2,525 \cdot 10^3$
CO		$1,982 \cdot 10^1$	$5,636 \cdot 10^0$	$1,978 \cdot 10^1$	$2,067 \cdot 10^0$	$1,978 \cdot 10^1$	$1,060 \cdot 10^{-7}$
CO ₂	$5,148 \cdot 10^{-3}$	$8,418 \cdot 10^0$	$2,260 \cdot 10^1$	$8,426 \cdot 10^0$	$2,617 \cdot 10^1$	$8,426 \cdot 10^0$	$2,824 \cdot 10^1$
O ₂	$3,595 \cdot 10^1$	$2,092 \cdot 10^{-2}$	$3,949 \cdot 10^0$	$2,174 \cdot 10^{-2}$	$6,065 \cdot 10^0$	$2,174 \cdot 10^{-2}$	$5,495 \cdot 10^0$
SO ₂		$2,930 \cdot 10^{-2}$	$1,150 \cdot 10^{-2}$	$3,600 \cdot 10^{-3}$	$8,227 \cdot 10^{-3}$	$3,600 \cdot 10^{-3}$	$8,249 \cdot 10^{-8}$
CaSO _{4/c}		$1,166 \cdot 10^{-1}$	$1,334 \cdot 10^{-1}$	$1,344 \cdot 10^{-1}$	$1,367 \cdot 10^{-1}$	$1,344 \cdot 10^{-1}$	$1,448 \cdot 10^{-1}$
Na ₂ SO _{4/c}		$6,233 \cdot 10^{-3}$	$6,233 \cdot 10^{-3}$	$6,233 \cdot 10^{-3}$	$6,233 \cdot 10^{-3}$	$6,233 \cdot 10^{-3}$	$6,224 \cdot 10^{-3}$
K ₂ SO _{4/c}		$1,474 \cdot 10^{-3}$	$2,578 \cdot 10^{-3}$	$7,586 \cdot 10^{-4}$	$2,541 \cdot 10^{-3}$	$7,586 \cdot 10^{-4}$	$2,608 \cdot 10^{-3}$
NO		$8,200 \cdot 10^{-4}$	$1,200 \cdot 10^{-3}$	$2,400 \cdot 10^{-3}$	$5,064 \cdot 10^{-3}$	$1,600 \cdot 10^{-3}$	$8,200 \cdot 10^{-4}$
NO ₂		$2,309 \cdot 10^{-5}$	$1,343 \cdot 10^{-3}$	$2,397 \cdot 10^{-5}$	$7,976 \cdot 10^{-4}$	$2,397 \cdot 10^{-5}$	$5,339 \cdot 10^{-5}$
NaNO ₂		$1,709 \cdot 10^{-11}$	$1,711 \cdot 10^{-11}$	$1,704 \cdot 10^{-11}$	$1,695 \cdot 10^{-11}$	$1,704 \cdot 10^{-11}$	$1,493 \cdot 10^{-6}$
KNO ₂		$3,756 \cdot 10^{-5}$	$2,914 \cdot 10^{-5}$	$1,700 \cdot 10^{-7}$	$1,679 \cdot 10^{-4}$	$1,700 \cdot 10^{-7}$	$2,882 \cdot 10^{-6}$

According to (7), the change in the number of moles of SO₂ is equal to the change in the number of moles of CaSO_{4/c}, which was taken into account when setting constraints (9). According to the calculation results, Table 2 is compiled, which presents 7 states of the system (from 0 to 6): 1 – characterizes the initial composition (y); 0, 2, 4 – modeling a system with constraints for the formation of NO and SO₂; 3 – without restrictions; 5 – close to state 2, but with a change in ψ ; 6 – the state of final equilibrium.

Comparison of states 0, 2, 4 shows that with a decrease in SO₂, CaSO_{4/c} increases and the O₂ content decreases. From the comparison of the results, it can be seen that the enthalpy (H) in states 0, 4, 5 remains approximately constant, while in state 2 it decreases noticeably. Close values of H indicate that an increase in NO is compensated by a decrease in SO₂ (an increase in CaSO_{4/c}). The exception from this series state 2 can be explained by various reasons: inaccuracy of measurements, fluctuations in the material and energy balances of the combustion zone, etc. Even small changes in concentrations of either NO or SO₂ (CaSO_{4/c}) can greatly change the enthalpy of the system (compare states 2 and 5). State 5 is conditional, because it has a value of φ 25% greater than in state 2.

Thus, the results obtained confirm the authors' assumption that the inverse dependences of NO and SO₂ on the molar ratio Ca/S [9] are explained by the

multidirectional energy flows of the reactions of CaSO_{4/c} and NO formation.

3 Conclusions

It is found that the alkali metals of the mineral part of the fuel (Ca, Na, K) can interact with both nitrogen and sulfur, affecting the formation of both NO and SO₂.

It is shown that further study and control of emissions of not only NO_x, but also sodium and potassium nitrites is necessary during the combustion of KAC.

It is clarified that for all the considered KAC (regardless of the content of sulfur and alkali metals), the temperature interval of the transition of condensed calcium sulfate to sulfur dioxide remains approximately constant (1400-1500K), and the transition process thermodynamically does not significantly depend on α .

A conclusion was made about the thermodynamic possibility of a simultaneous increase in NO_x formation and a decrease in SO₂, which is due to multidirectional energy flows during the formation of CaSO_{4/c} and NO.

The conclusions obtained, of course, require additional verification.

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