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Thermodynamic modeling of interaction of aluminous ashes with carbonates

There was obtained the equilibrium phase composition for systems of mullite-sodium carbonate-calcium carbonate, sillimanite-sodium carbonate-calcium carbonate, ash-sodium carbonate-calcium carbonate at different variations of relations of Na_2O/Al_2O_3, CaO/SiO_2, CaO/Al_2O_3. The optimal temperature range for the interaction of aluminous ashes with carbonates was determined.

Key words: sintering products, aluminous ashes, mullite, sillimanite, nepheline, gehlenite, tricalcium aluminate, tricalcium silicate, tricalcium aluminum silicate.

The urgency of solving the problem of ash processing forming at combustion of coal in thermal power plants increases due to the continuing pace of consumption of coal and increase of the proportion of low-grade coal in the overall balance of coal mining. Ashes of thermal power plants are complex materials by their composition. They are characterized by high content of alumina (24–35 %) and silica (55–60 %), relatively low content of iron and calcium oxides. They may relate to the aluminous type. Aluminium oxide is combined to form mullite ($3Al_2O_3 \cdot 2SiO_2$) and partially to form sillimanite ($Al_2O_3 \cdot SiO_2$) according to X-ray and crystal optic analysis.

Thermodynamic analysis of systems, modeling the sintering of alumina ashes of thermal power plants with sodium and calcium carbonates, was performed using computer software and the automated system of thermodynamic data and calculations of equilibrium states «ASTC» [1, 2].

The task of the thermodynamic analysis was to determine the equilibrium parameters of the system. The conditions of optimization of the future technological process were determined by varying the conditions of the initial state of the thermodynamic system (the content of chemical elements and the values of two specified characteristics).

The automated system of thermodynamic data and calculations of equilibrium states «ASTC» is based on the principle of maximum entropy of an isolated thermodynamic system that has a number of advantages in a logical, methodological and practical level compared to other methods of calculating the equilibrium states, in particular, to the method based on the law of mass action which makes it necessary to use values of equilibrium constants of chemical reactions in calculations [3, 4].

The Lagrangian function is used to solve the problem of finding the extreme thermodynamic entropy in relation to the degree of freedom which includes the concentration of the equilibrium mixture components, temperature and pressure. Certain restrictions were imposed at finding extreme values on the unknowns. The resulting system of equations is solved using the Newton's method which is the method of successive approximations.

The algorithm provides for the formation of the software design of the system of equations and, therefore, allows the calculation of equilibrium for an arbitrary set of chemical elements and components forming the system. The mathematical model is built for complex multi-component systems which include individual gas and condensed chemicals and their solutions. The initial content of chemical elements and the numerical value of the two thermodynamic parameters were given to characterize the equilibrium state of the system studied. An isolated or a closed system in which a balance is achieved through the internal phase and chemical transformations is considered to find the extremum of entropy. Mechanical and energy balance with the environment is presupposed to be reached. It is assumed that the system under study is heterogeneous, consisting of several homogeneous parts of certain visible boundaries. Thus all individual gaseous substances are in the same gas phase and condensed material may form a separate phase and the condensed solution. Number of condensed solutions is limited to two, so as not to complicate the algorithm.

Database of the thermodynamic data of substances properties of the «ASTC» program whose formation is possible in the system under the specified conditions is used to obtain the results.

There were calculated the equilibrium parameters and the equilibrium phase composition of systems with different molar ratios of Na_2O/Al_2O_3 and CaO/Al_2O_3:

1) $3Al_2O_3 \cdot 2SiO_2$–Na_2CO_3–$CaCO_3$;

2) $Al_2O_3 \cdot SiO_2$–Na_2CO_3–$CaCO_3$.

The calculations are performed in the temperature range 473–1673 K at 1 atm pressure. Thermodynamic data for the calculations are taken from reference books.

The initial composition of the systems is shown in the Table 1.

Table 1

The initial phase composition

Number of composition	The components content, %			
	Al_2O_3	SiO_2	Na_2CO_3	$CaCO_3$
1	26.75	10.49	27.80	34.96
2	14.01	16.48	14.56	54.94

Initial concentrations of sodium carbonate and calcium carbonate correspond to stoichiometric quantities of aluminosilicates decomposition according to the reactions:

$$3Al_2O_3 \cdot 2SiO_2 + 3Na_2CO_3 + 4CaCO_3 \rightarrow 3(Na_2O \cdot Al_2O_3) + 2(2CaO \cdot SiO_2) + 7CO_2\uparrow$$

$$Al_2O_3 \cdot SiO_2 + Na_2CO_3 + 2CaCO_3 \rightarrow Na_2O \cdot Al_2O_3 + 2CaO \cdot SiO_2 + 3CO_2\uparrow$$

It was interesting to obtain the thermodynamic characteristics of mullite heating in the absence of sodium and calcium carbonates. The results of the thermodynamic analysis of the process of the mullite heating are given in Fig. 1. Consideration of the results is showed that two phases Al_2O_3 and $Al_2O_3 \cdot SiO_2$ are at equilibrium in the temperature range 573–1173 K. At temperatures above 1173 K mullite is formed which is thermodynamically stable compound.

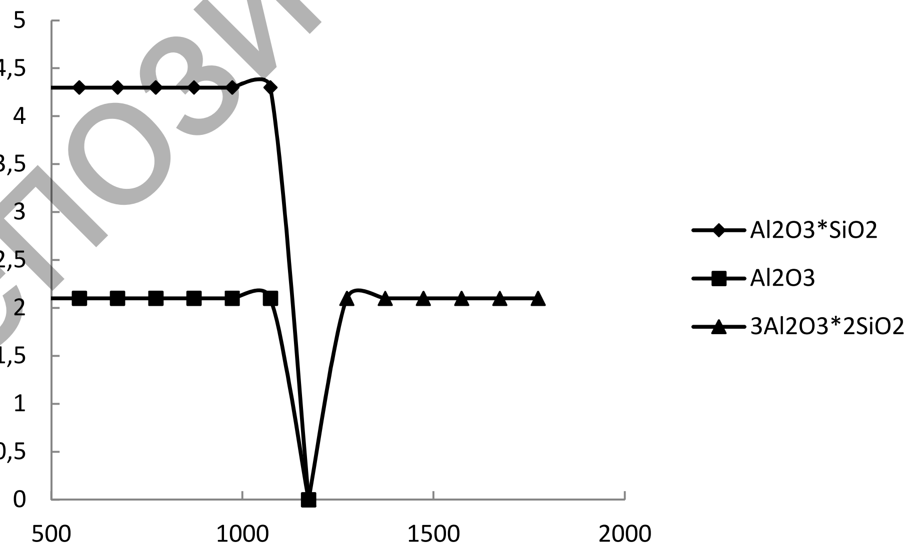


Figure 1. The phase composition of mullite thermal heating

The data on the thermodynamic modeling of the system 1 are shown by the values of the equilibrium phase composition (Fig. 2). From figure 2 it follows that in this system in the temperature range 673–973 K mullite reacts with sodium carbonate to form $NaAlSiO_4$.

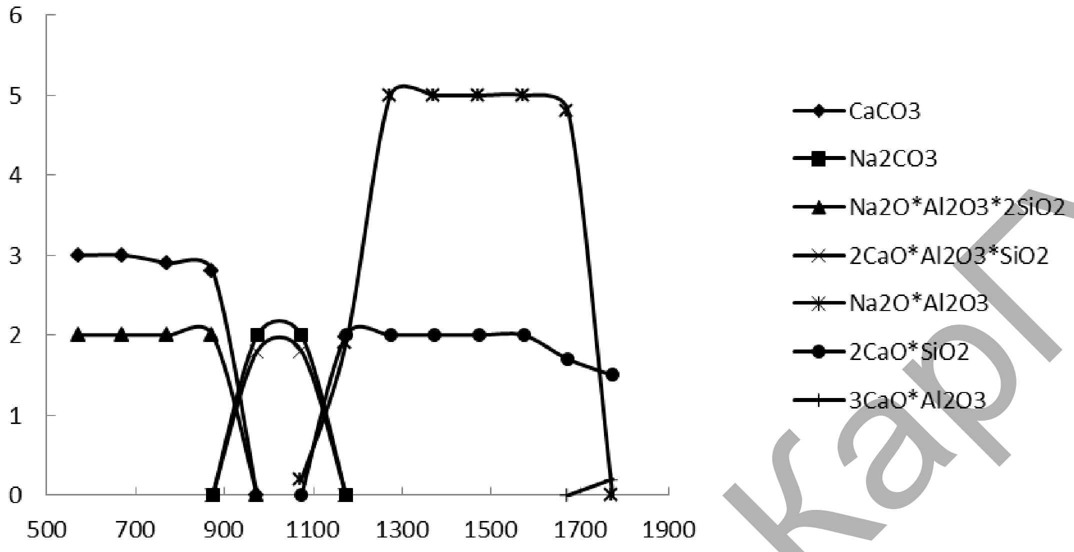


Figure 2. The dependence of the equilibrium phase composition of mullite-sodium-calcium carbonate from the sintering temperature

Such conversion is explained by features of the crystal structure of mullite which is close to the structure of sillimanite. The structure is paired chains $[SiO_2O_5]_\infty$ where Si^{4+} ion partially substituted for isomorphic aluminum ion Al^{3+}. In turn, mullite has an aluminum ion as six-$[AlO_6]$, and fourfold-$[AlO_4]$ coordination on oxygen. The lattice of mullite is constructed of $[AlO_4]$, $[AlO_6]$ groups and $[SiO_4]$ island groups. The structural formula of mullite is as follows $Al_4^{VI}O_3[Al^{V}Si_2O_5]_2$ or $Al_4^{VI}[Al^{IV}(Si_2Al^{IV})O_{13}]$ [5].

There are voids with radius 0.67 nm in the lattice of mullite. The ions of the smaller and close ionic radius (Ca^{2+} и Na^{+}) can penetrate in to the voids, resulting in destruction of the lattice and formation of mullite and nepheline at a temperature below 673 K by reacting with sodium carbonate.

When the sintering temperature is increased up to 773 K nepheline interacts with calcium carbonate to form gehlenite ($2CaO\cdot Al_2O_3\cdot SiO_2$) by reacting:

$$Na_2O\cdot Al_2O_3\cdot SiO_2 + 4CaCO_3 \rightarrow 2CaO\cdot Al_2O_3\cdot SiO_2 + 2CaO\cdot SiO_2 + Na_2CO_3 + 3CO_2\uparrow$$

Gehlenite which is stable in the temperature range 873–1073 K is fully decomposed with sodium carbonate at 1173 K with the formation of the main products such as sodium aluminate and dicalcium silicate according to the reaction:

$$2CaO\cdot Al_2O_3\cdot SiO_2 + Na_2CO_3 \rightarrow Na_2O\cdot Al_2O_3 + 2CaO\cdot SiO_2 + 3CO_2\uparrow$$

There is a wide region of stability of sodium aluminate and dicalcium silicate from 1173 to 1573 K. When the temperature rises to 1673 K staple sintering products interact to form secondary phases such as tricalcium aluminate ($3CaO\cdot Al_2O_3$) and nepheline ($NaAlSiO_4$). Occurrence in equilibrium sinter of sintering byproducts leads to reduction of sodium aluminate phase which is soluble in an alkaline solution. Consequently, the sintering byproducts formation is undesired because aluminum oxide is hardly to be isolated by leaching as evidenced by the paper [6], in which the author indicates a significant reduction in the degree of extraction of alumina by leaching with soda alkaline solutions, in case the sintering process of high silicon-containing aluminum containing raw materials by soda and limestone is carried out at high temperatures 1573–1698 K.

The results of thermodynamic simulation of system 2 are shown in Figure 3. It shows the equilibrium phase composition. Processes occurring during sintering sillimanite with sodium and calcium carbonate are similar to the described above for mullite. Basic products of sintering which are dicalcium aluminate and sodium silicate are produced at 1073 K. They are stable in the temperature range of 1173–1573 K. At 1673, 1773 K dicalcium aluminate interacts with sodium silicate to form nepheline, tricalcium aluminate and a new phase sodium silicate ($Na_2O\cdot SiO_2$).

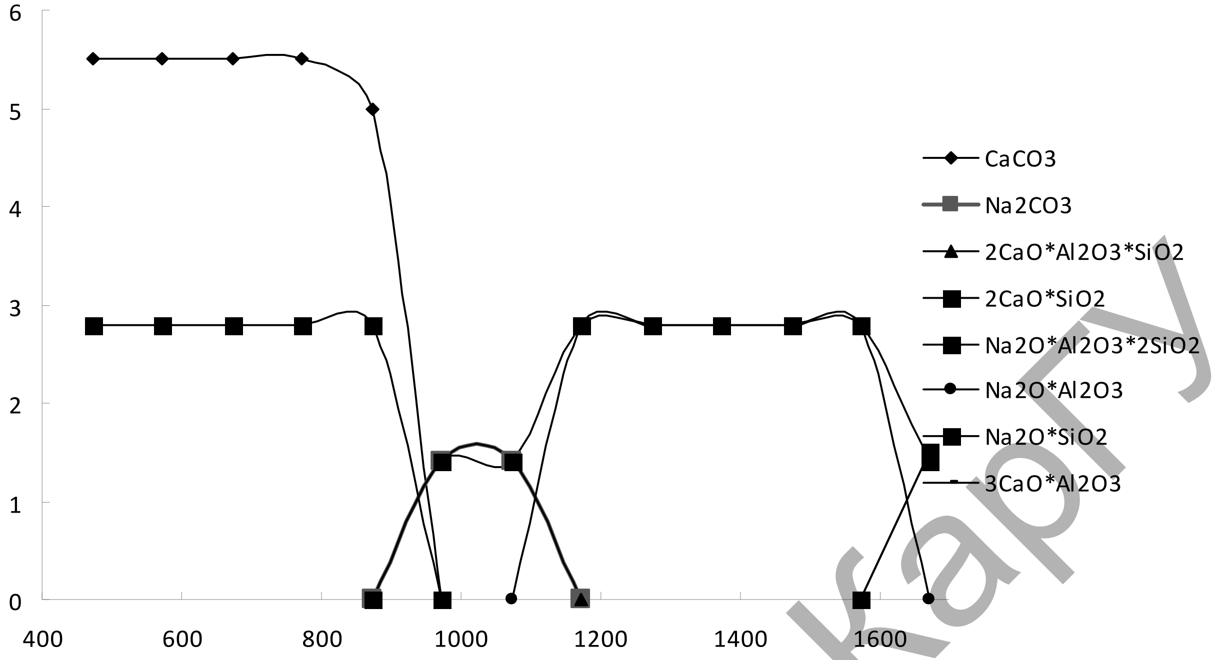


Figure 3. The dependence of the equilibrium phase composition
of the sillimanite-sodium carbonate-calcium carbonate system on the sintering temperature

It was calculated the initial phase composition of the model system with molar ratios of Na_2O/Al_2O_3 = 0.7–1.0, CaO/SiO_2 = 2, CaO/Al_2O_3 = 1–0.3, CaO/Fe_2O_3 = 1 based on the chemical composition of coal ash (24.77 % Al_2O_3, 49.4 % SiO_2, 7.34 % Fe_2O_3, 1.58 % CaO).

The equilibrium phase composition of the system ash – sodium carbonate – calcium carbonate were calculated in the temperature range 573–1673 K at a pressure of 1 atm and variations of the initial composition of the system. The initial composition is shown in the Table 2.

Table 2

The initial composition of the system ash – sodium carbonate – calcium carbonate

No. of composition	Molar relation Na_2O/Al_2O_3	Molar relation CaO/Al_2O_3	Content of the components, mass, %					
			Al_2O_3	SiO_2	Fe_2O_3	CaO	$CaCO_3$	Na_2CO_3
1	1.00	-	8.89	17.72	2.63	0.57	60.93	9.25
2	0.90	0.10	8.89	17.74	2.63	0.57	62.76	7.41
3	0.80	0.20	8.85	17.56	2.61	0.56	63.01	6.42
4	0.70	0.30	8.81	17.56	2.61	0.56	63.39	5.10

Making calculations it was taken into account the formation of these condensed phases:

$2CaO{\cdot}Al_2O_3{\cdot}SiO_2$, $3CaO{\cdot}Fe_2O_3{\cdot}2SiO_2$, $3CaO{\cdot}2SiO_2$, $Na_2O{\cdot}SiO_2$, $CaO{\cdot}Al_2O_3{\cdot}2SiO_2$, $CaO{\cdot}Al_2O_3$, $3CaO{\cdot}Al_2O_3$, $CaO{\cdot}SiO_2$, $2CaO{\cdot}SiO_2$, $CaO{\cdot}Fe_2O_3$, $2CaO{\cdot}Fe_2O_3$, $Na_2O{\cdot}Fe_2O_3$, $Na_2O{\cdot}Al_2O_3$, $Na_2O{\cdot}Al_2O_3{\cdot}2SiO_2$. The gaseous components included are as follows CO_2, CO, O_2, O, Na, Na_2O, NaO, SiO_2, AlO, Al_2O.

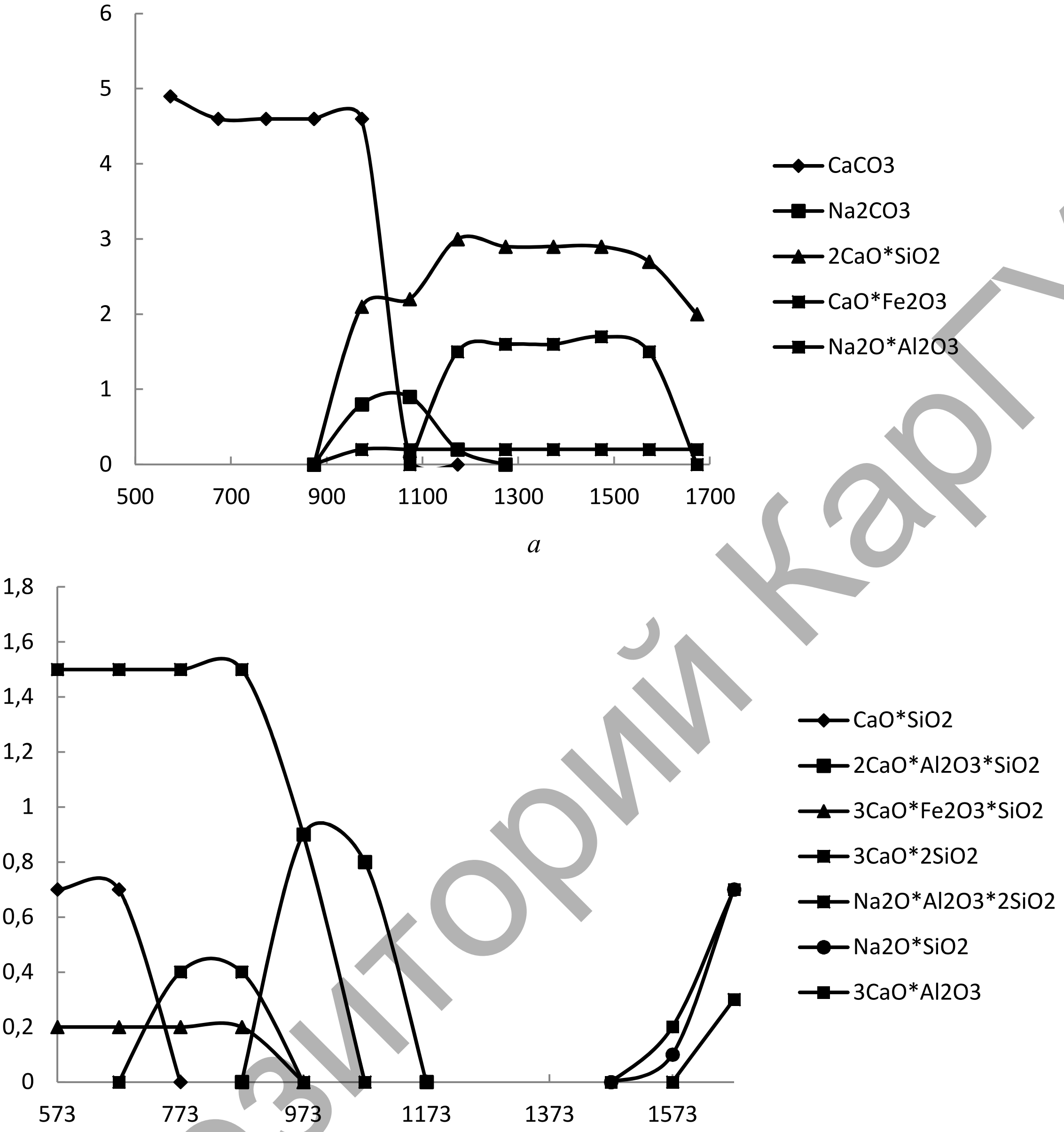
Initial concentrations of sodium and calcium carbonate correspond to stoichiometric reactions:
Composition 1.

$$3Al_2O_3{\cdot}2\ SiO_2 + Fe_2O_3 + 3Na_2CO_3 + 5CaCO_3 \rightarrow$$
$$\rightarrow 3(Na_2O{\cdot}Al_2O_3) + 2(2CaO{\cdot}SiO_2) + CaO{\cdot}Fe_2O_3 + 8CO_2\uparrow$$

Composition 2–5.

$$3Al_2O_3{\cdot}2SiO_2 + Fe_2O_3 + 2Na_2CO_3 + 6CaCO_3 \rightarrow$$
$$\rightarrow 2(Na_2O{\cdot}Al_2O_3) + 2(2CaO{\cdot}SiO_2) + CaO{\cdot}Al_2O_3 + CaO{\cdot}Fe_2O_3 + 8CO_2\uparrow$$

Figure 4 (a, b) shows the equilibrium phase composition of the system: ash – sodium carbonate – calcium carbonate in a molar ratio Na_2O/Al_2O_3 = 1, CaO/Al_2O_3 = 2, CaO/Fe_2O_3 = 1.



a

b

Figure 4. The dependence of the content of main products (*a*) and byproducts of sintering of the system 1 at $Na_2O/Al_2O_3 = 1$ from the sintering temperature

We can see from these data that nepheline ($Na_2O{\cdot}Al_2O_3{\cdot}2SiO_2$) is formed at 573 K in the interaction of mullite with sodium and calcium carbonate. Calcium silicate ($CaO{\cdot}SiO_2$) is formed alongside with nepheline. Tricalcium silicate ($3CaO{\cdot}2SiO_2$) is formed by further interaction of $CaCO_3$ with $CaO{\cdot}SiO_2$. Monocalcium and tricalcium silicates are absent at 873 K.

At 573–773 K soda reacts with silica to form sodium silicate which gives an alumina polybasic sodium aluminosilicate at a slight increase in temperature:

$$Na_2O{\cdot}Al_2O_3 + Al_2O_3 \rightarrow 2Na_2O{\cdot}Al_2O_3{\cdot}2SiO_2$$

The last one at further heating reacts with alumina to form sodium aluminum silicate and sodium aluminate:

$$2Na_2O{\cdot}Al_2O_3{\cdot}2SiO_2 + Al_2O_3 \rightarrow Na_2O{\cdot}Al_2O_3{\cdot}2SiO_2 + Na_2O{\cdot}Al_2O_3$$

At 973 K the reaction proceeds between nepheline and calcium carbonate to give gehlenite ($2CaO{\cdot}Al_2O_3{\cdot}SiO_2$) and release sodium carbonate in a separate phase which is in equilibrium prior to 1073 K. Besides, at this temperature calcium ferrite is formed ($CaO{\cdot}Fe_2O_3$).

Double iron and calcium silicate ($3CaO\cdot Fe_2O_3\cdot 2SiO_2$) is an intermediate compound formed. Double calcium and iron silicate is stable in the range of 573–873 K but it decomposes at 973 K by reacting with calcium carbonate by the reaction:

$$3CaO\cdot Fe_2O_3\cdot 2SiO_2 + 2CaCO_3 \rightarrow CaO\cdot Fe_2O_3 + 2(2CaO\cdot SiO_2) + 2CO_2\uparrow$$

Calcium ferrite is a stable compound from 973 to 1673 K. As can be seen from figure 4*a* one of the main reaction products dicalcium silicate is formed at 973 K and sodium aluminate is formed at 1173 K by the reaction:

$$2CaO\cdot Al_2O_3\cdot SiO_2 + Na_2CO_3 \rightarrow Na_2O\cdot Al_2O_3 + 2CaO\cdot SiO_2 + 2CO_2\uparrow$$

The equilibrium phase composition of sintering product is presented only by sodium aluminate, dicalcium silicate and calcium ferrite in the range of 1173–1573 K. Sodium silicate, tricalcium aluminate and nepheline are formed with increasing temperature up to 1673 K. Al_2O_3 does not pass in to the solution by further soda-alkali leaching of these products.

The resulting calculation of the equilibrium phase composition of the system is confirmed by the results of X-ray analysis of ash cakes with sodium and calcium carbonate. The main phase of the cake according to the X-ray diffraction at 873 K is calcite ($CaCO_3$) and nepheline ($Na_2O\cdot Al_2O_3\cdot 2SiO_2$), calcite, gehlenite, dicalcium silicate at 973 K, dicalcium silicate, sodium aluminate, at 1073 K, sodium aluminate ($Na_2O\cdot Al_2O_3$), β-dicalcium silicate ($2CaO\cdot SiO_2$) at 1573 K.

The identity of the experimental and predicted by thermodynamic model phase compositions confirms the conclusions of the thermodynamic analysis of the formation of intermediate compounds $Na_2O\cdot Al_2O_3\cdot 2SiO_2$, $2CaO\cdot Al_2O_3\cdot SiO_2$ in the temperature range 873–1273 K, the main products of sintering $Na_2O\cdot Al_2O_3$, $2CaO\cdot SiO_2$ in the temperature range 1173–1573 K and byproducts $3CaO\cdot Al_2O_3$, $Na_2O\cdot SiO_2$, $Na_2O\cdot Al_2O_3\cdot 2SiO_2$ at 1673 K in the interaction of aluminum ash containing sodium and calcium carbonates.

The equilibrium phase compositions (formulations 2–4) in a molar ratio $Na_2O/Al_2O_3 = 0.90–0.70$ were calculated. At reducing Na_2O/Al_2O_3 molar ratio from 0.90 to 0.70 increase of $CaCO_3$ content was calculated accordingly to the total binding of aluminate in an aluminum sintering product to form sodium and calcium aluminate.

With increasing content of calcium carbonate in the initial phase composition amount of sodium aluminate formed decreases at $Na_2O/Al_2O_3 = 1.00$ from 1.70 mol/kg to 1.60 mol/kg at $Na_2O/Al_2O_3 = 0.9$. At the same time a new phase calcium aluminate ($CaO\cdot AlO_3$) is formed which is stable at 973–1173 K. Calcium aluminate transforms into tricalcium aluminate ($3CaO\cdot Al_2O_3$) at 1273 K.

Tricalcium aluminate is sparingly soluble in sodium carbonate solution in the leaching process, and during its formation degree of leaching will be reduced in the equilibrium phase composition, so the formation of its is undesirable. Amount of dicalcium silicate decreases from 2.95 mol/kg $Na_2O/Al_2O_3 = 1$ to 2.45 mol/kg $Na_2O/Al_2O_3 = 0.9$.

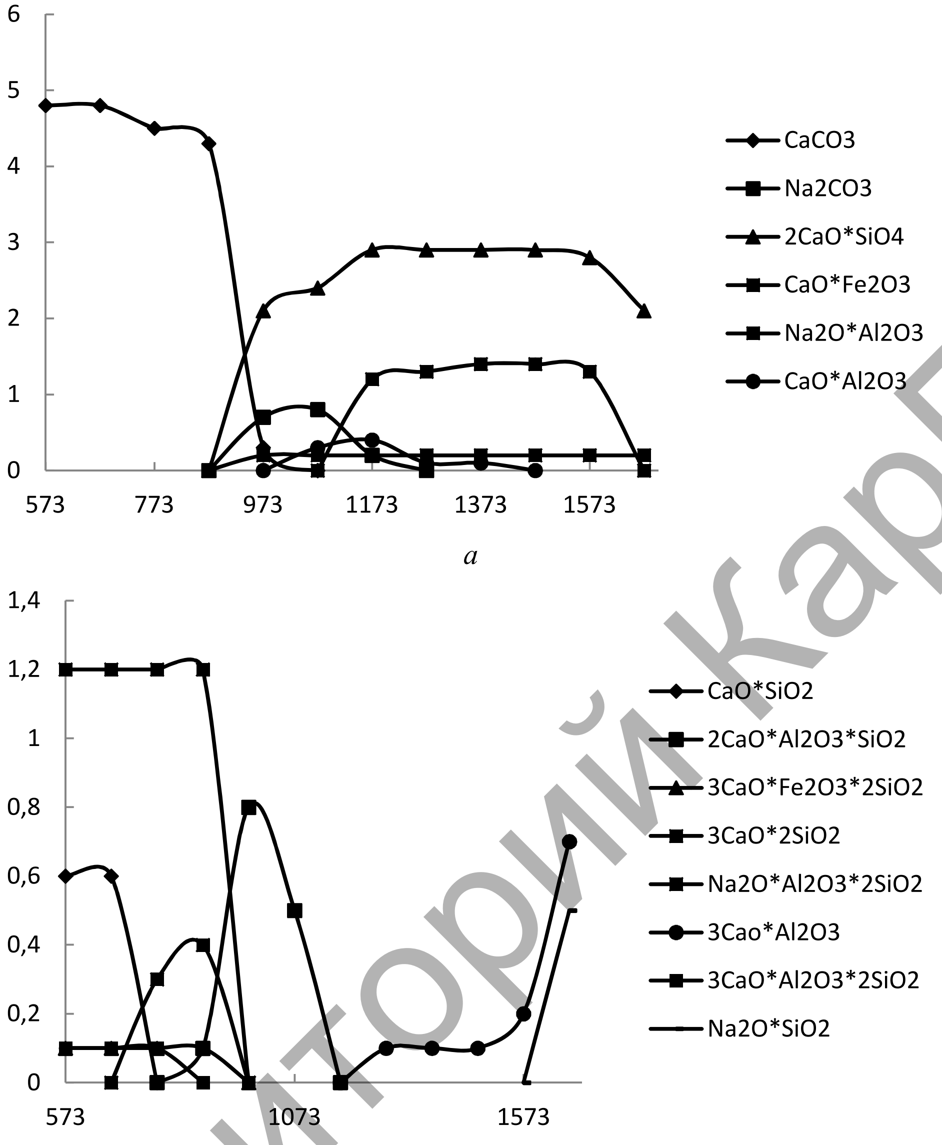
In thermodynamic analysis of the composition 2 amount of nepheline decreases accordingly from 1.8 mol/kg to 1.6 mol/kg at 573 to 873 K as the amount of sodium carbonate was introduced less than one.

With further decrease in the amount of sodium carbonate in the initial phase 3 amount of sodium aluminate is reduced to 1.45 mol/kg. At the same time the temperature range of stability of sodium aluminate (973–1473 K) is increased in an equilibrium process of interaction (Fig. 5*a*, *b*). Tricalcium aluminum silicate ($3CaO\cdot Al_2O_3\cdot SiO_2$) forms at 573 K. It transforms into calcium aluminate at 973 K.

Phase composition of the system 4 compared with the composition 3 is not significantly changed, but the amount of the main reaction product sodium aluminate decreases to get the value 1.25 mol/kg, the content of dicalcium silicate remains constant.

In contrast to the composition 1 the condensed phase of nepheline is missing in phase compositions 2–4 at 1573 1673 K. Calcium ferrite content remains unchanged; for all compositions it is 0.15 mol/kg.

The results of thermodynamic calculations of the interaction of ash with sodium and calcium carbonate showed that the main factors affecting the equilibrium phase composition of the reaction products are the temperature and the content of sodium and calcium carbonates in the studied system.



a

b

Figure 5. Dependence of the major (*a*) and side (*b*) sintering products of system 3 at $Na_2O/Al_2O_3 = 0.8$ from the sintering temperature

Data of thermodynamic analysis of the system ash – sodium carbonate – calcium carbonate (formulations 1–4) allowed determining the optimal temperature range interactions which is amounted to 1173–1573 K.

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Р.К.Сотченко

Алюминий күлінің карбонаттармен әрекеттесуін термодинамикалық модельдеу

Na_2O/Al_2O_3, CaO/SiO_2, CaO/Al_2O_3 әр түрлі вариациялық қатынас кезінде болатын муллит – натрий карбонат – кальций карбонаты, силлиманит – натрий карбонат – кальций карбонаты, күл – натрий карбонат – кальций карбонаты жүйесінің фазалық тепе-теңдік құрамы алынды. Саз балшықты күлдің карбонаттармен әрекеттесудегі оңтайлы температуралық аралық анықталды.

Р.К.Сотченко

Термодинамическое моделирование взаимодействия алюминийсодержащих зол с карбонатами

Получены равновесные фазовые составы систем муллит – карбонат натрия – карбонат кальция, силлиманит – карбонат натрия – карбонат кальция, зола – карбонат натрия – карбонат кальция при различных вариациях соотношений Na_2O/Al_2O_3, CaO/SiO_2, CaO/Al_2O_3. Определен оптимальный температурный интервал взаимодействия глиноземистых зол с карбонатами.