Thermochemical activation of hydrated aluminosilicates and its importance for alumina production

O. A. Dubovikov, Professor, Department of Chemical Technologies and Energy Carrier Processing[1]
V. N. Brichkin, Head of Department of Metallurgy[1], e-mail: kafmet@spmi.ru
A. D. Ris, Post-Graduate Student, Department of Metallurgy[1]
A. V. Sundurov, Post-Graduate Student, Department of Metallurgy[1]

[1] Saint-Petersburg Mining University, St. Petersburg, Russia.
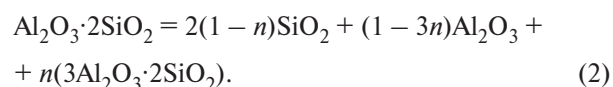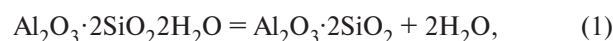
It is demonstrated that activation of minerals of kaolin and chamosite series is based on their thermodynamic unsteadiness with reference to thermal dissociation with formation of amorphous silicon oxide and aluminium as primary products followed by generation of mullite and crystalline modifications of oxides as steady final products. This provides a technological basis of partial silicon and aluminium separation along with rising the silicon module of thermochemical treatment products until the values, acceptable for alumina production by alkaline methods. Adduced are the diagrams of kaolin and chamosite phase transformation on thermal treatment as well as design dependences of the silicon module value of thermochemical processing products upon mullitization degree of the products and the value of silica chemical extraction into alkaline solution. Listed are the results of experimental study of chemical and phase composition of chamosite samples with different iron oxidability level. It is established an essential difference in activity of natural chamosite forms and the probes after heat treatment. It is shown that chamosite oxidability level, temperature and duration of heat treatment resulting in differences of mullitization degree of the products, as well as indices of silica chemical extraction on hydrochemical treatment of activated materials are the significant factors of separation of silicon and aluminium oxides. Proposed are the techniques of thermochemical activation of low-grade bauxites, containing minerals of kaolin and chamosite groups, which are realized in the form of the principal schematic apparatus and process diagram, possessing the required adaptation rate to alumina manufacturing by alkaline methods.

Key words: kaolin, chamosite, bauxites, silicon module, activation, heat treatment, selective leaching.
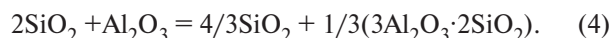***DOI:*** 10.17580/nfm.2018.02.02

Kaolin and its analogues are among well-known and widespread minerals, which are used since antiquity and importance of which doesn't lessen until now; moreover, in certain domains their significance makes distinct progress. Realistically, among such spheres are production of refractory products, building materials, cementitious compositions, fillers and pigments. One can also consider kaolin ores as a low-grade aluminiferous raw material of regional importance [1]. Such interest to kaolin raw material is explained not only by the fact that clays is an exceptionally widely spread rock consisting mainly from the minerals of subclass of layered silicates, but a series of in-demand properties, such as plasticity, low abrasivity, chemical and thermal steadiness, acceptable for alumina production Al_2O_3 content up to 39.5% and capability for generation of chemically active products at relatively low temperatures. At the same time, it is necessary to draw attention to a possibility of hydrothermal modification of kaolin, which makes it possible to use this phenomenon in the clays beneficiation process [2], and its thermal decomposition in a temperature range from 600 to 900 ºC, resulting in formation of active forms of metakaolin and silica according to the following reactions:

$$Al_2O_3 \cdot 2SiO_2 2H_2O = Al_2O_3 \cdot 2SiO_2 + 2H_2O, \qquad (1)$$

$$Al_2O_3 \cdot 2SiO_2 = 2(1 - n)SiO_2 + (1 - 3n)Al_2O_3 + n(3Al_2O_3 \cdot 2SiO_2). \qquad (2)$$

The first of the indicated processes allows obtaining of activated additions for mortar and dry construction mixes; the second one creates the necessary prerequisites for thermochemical beneficiation of highly kaolinitized materials, including loamy bauxites, which represents prospective kind of aluminiferous raw material [4−8]. Great importance of the mentioned processes has stipu-

lated the necessity of their thorough investigation, which has allowed one to gain modern ideas of mechanism of kaolin phase transformations on its thermal dissociation, Fig. 1 [9]. This allows to consider reaction (2) as a multi-stage process, which is connected in a low-temperature area with formation of amorphous forms of silica and aluminium oxide according to reaction (3) followed by generating thermodynamically resistant mullite by reaction (4):

$$Al_2O_3 \cdot 2SiO_2 = 2SiO_2 + Al_2O_3, \qquad (3)$$

$$2SiO_2 + Al_2O_3 = 4/3SiO_2 + 1/3(3Al_2O_3 \cdot 2SiO_2). \qquad (4)$$

Thus, equation (2) may be treated as intermediate state of a system with variable stoichiometry with respect to interaction products, corresponding to the current mullitization degree, for which quantity of Al_2O_3, converted from kaolin into mullite content may be used. At the same time, a distinction in chemical activity of the products regarding alkaline solutions creates the necessary prerequisites for selective silica extraction into solution and obtaining the concentrate with composition favourable for its consequent processing by pyro- and hydrometallurgical methods:

$$SiO_2 + 2NaOH = Na_2SiO_3 + H_2O. \qquad (5)$$
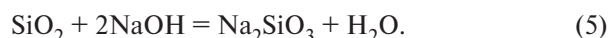
It is well known that silicon module serves as an overall quality index of aluminiferous raw material. With reference to the given figures of silica extraction and kaolin
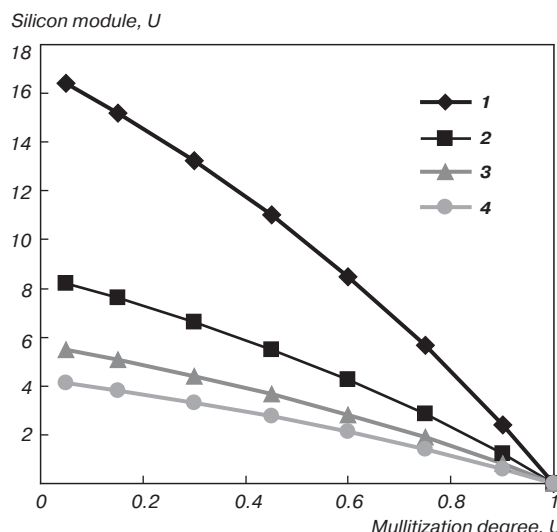

Fig. 2. The calculated silicon module $(\mu_{si})_{act}$ of kaolin heat treatment products according to equation (6) depending on its mullitization degree for the SiO_2 recovery into solution index (ε_{SiO_2}) by equation (5):
1 − 0.95; *2* − 0.9; *3* − 0.85; *4* − 0.8

mullitization degree, it may be calculated by the following equation providing the mullite inertness in subsequent engineering procedure [10]:

$$(\mu_{si})_{act} = 0.85(1 - 3n)/(1 - n)(1 - \varepsilon_{SiO_2}), \qquad (6)$$

where: μ_{si} − silicon module of material, i. e. Al_2O_3/SiO_2 mass ratio; n is a stoichiometric coefficient in equation (2), which is matched by a $3n$ kaolin mullitization degree at n
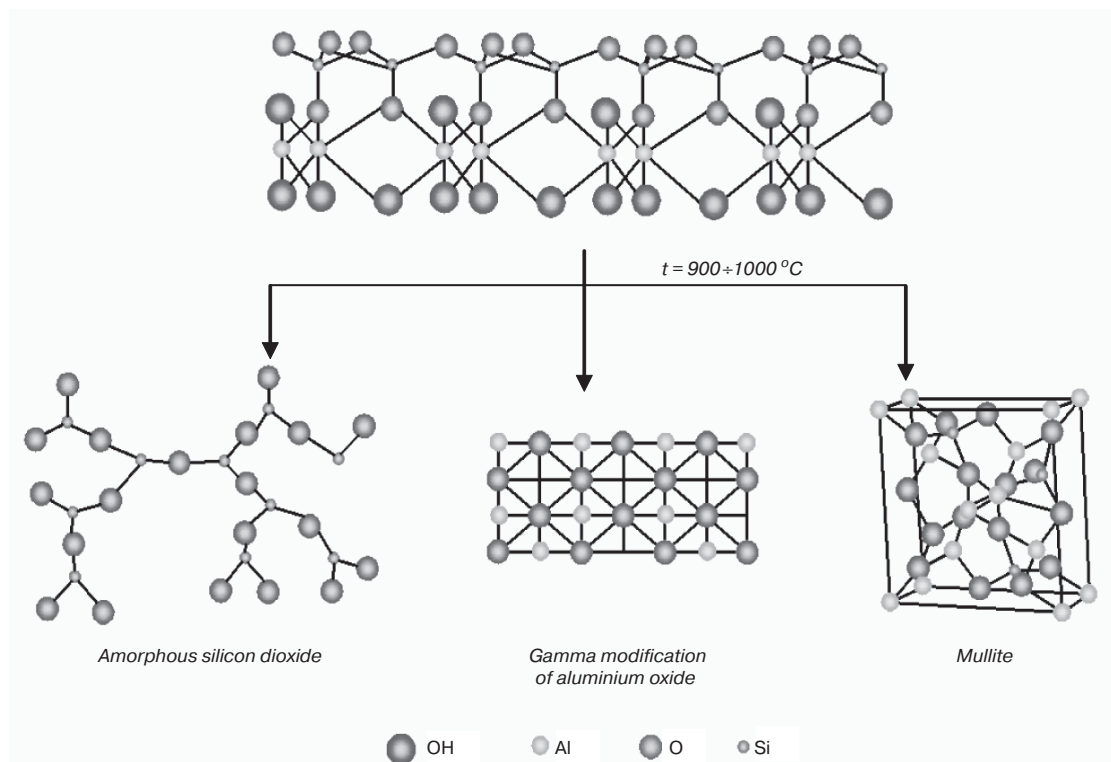

Fig. 1. Diagram of kaolin phase transformations during the process of heat treatment

from 0 to 1/3; ε_{SiO_2} — silica extraction into solution by equation (5).

The results of calculations according to the equation (6) are represented in Fig. 2, which allows one to suggest a theoretical possibility of essential increasing the silicon module of the thermochemical processing product with respect to initial kaolin value μ_{si}, which amounts to 0.85 U. for pure material. Since an active silica component in pyrometallurgical process of kaolin raw material processing is not an underextracted amorphous SiO_2 only, but silica being a part of mullite composition as well, than the silicon module value would be determined by the overall content of aluminium oxide and silicon oxide in the thermochemical processing product. Calculation of the silicon module total (gross) value by equitation (7) has been implemented on the analogy of calculations according to the equation (6), Fig. 3:

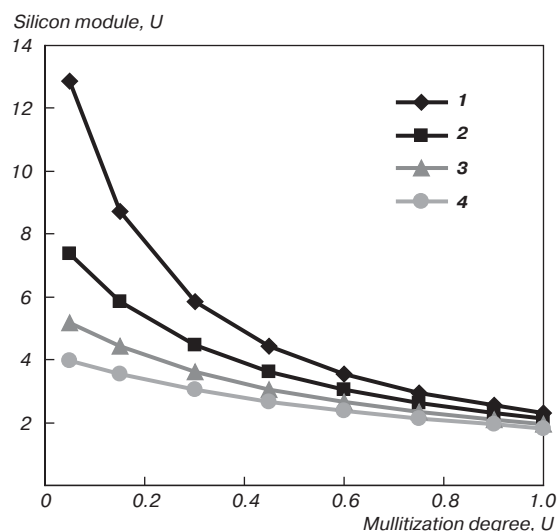$$(\mu_{si})_{gross} = 0.85/[(1 - \varepsilon_{SiO_2}(1 - n)]. \tag{7}$$

Fig. 3. The calculated silicon module $(\mu_{si})_{gross}$ of kaolin heat treatment products according to equation (7) depending on its mullitization degree for the SiO_2 recovery into solution index (ε_{SiO_2}) by equation (5):
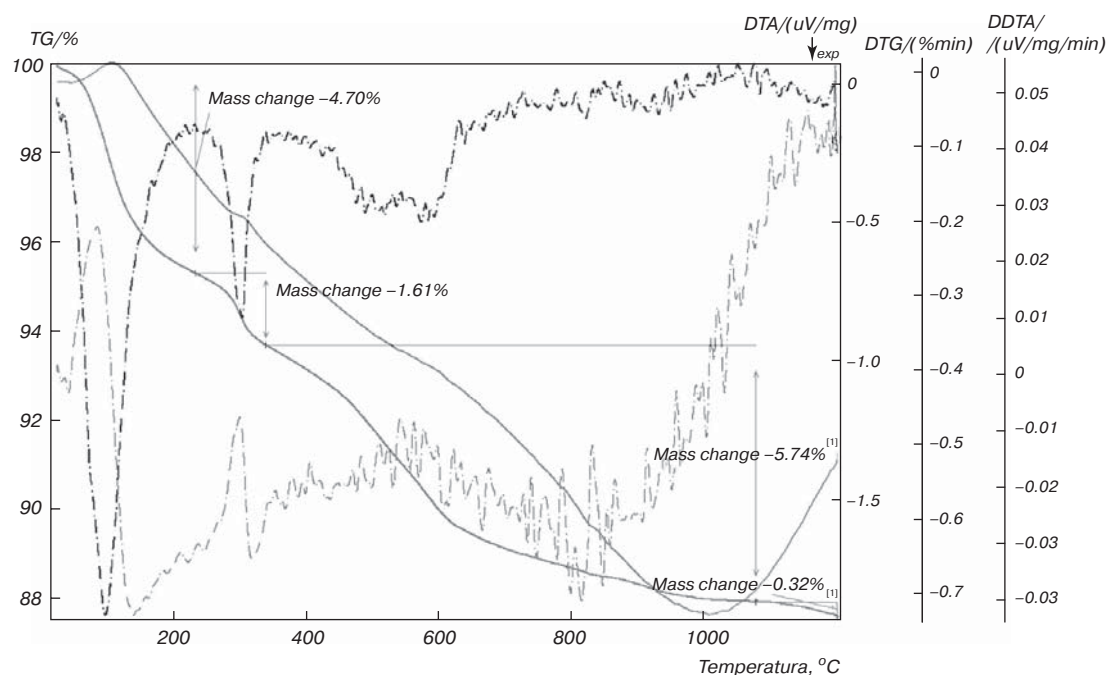$1 - 0.95$; $2 - 0.9$; $3 - 0.85$; $4 - 0.8$

Fig. 4. Results of the chamosite sample thermal analysis

Table 1

Chemical composition of the Kursk magnetic anomaly chamosite samples, which differ in the iron oxidability level

№	Content, wt.%							Oxidability level Fe^{+3}/Fe_{tot}	Modification ratio O/M**
	Al_2O_3	SiO_2	Fe_2O_3	FeO	R_2O*	TiO_2	Percent of other impurities		
1	31.75	26.00	14.65	8.43	0.25	1.96	15.58	0.61	2.00
2	21.70	12.53	31.53	24.17	0.15	1.02	10.08	0.54	2.00
3	18.26	15.30	28.03	29.61	0.16	1.19	8.08	0.46	1.75
4	19.17	18.32	24.18	27.70	0.32	1.19	7.24	0.44	4.00
5	23.72	22.40	17.26	23.30	0.20	0.61	10.52	0.40	9.00
6	37.74	20.20	7.09	24.01	1.05	1.86	9.10	0.21	3.00

*$R_2O = Na_2O + K_2O$;
**(O/M) — ratio in shares in a sample of chamosite modifications of different syngony — orthogonal / monoclinic.
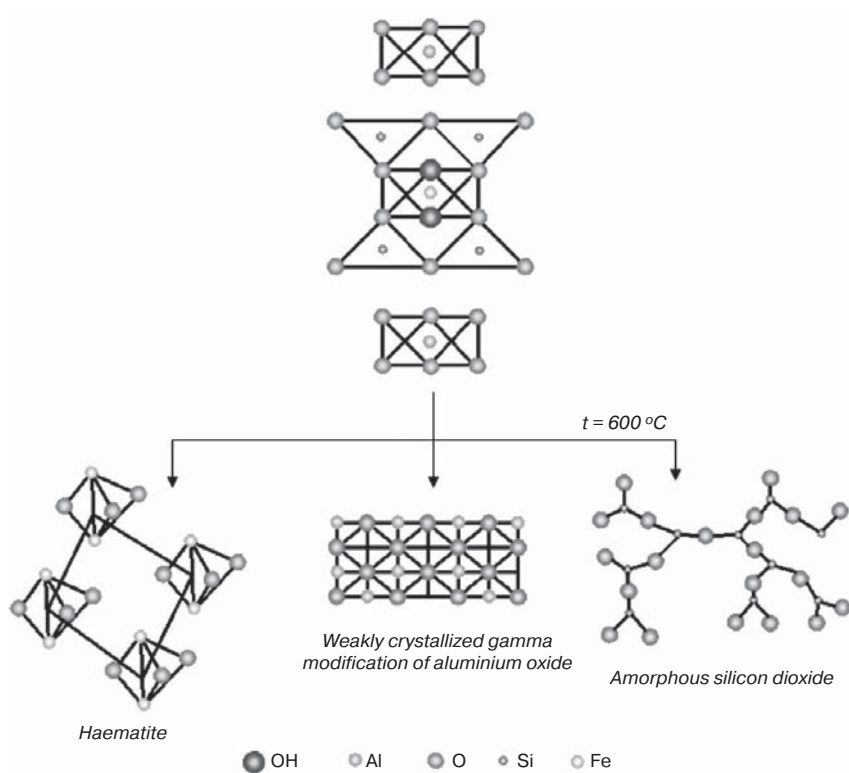
Fig. 5. Diagram of chamosite phase transformations during the process of heat treatment
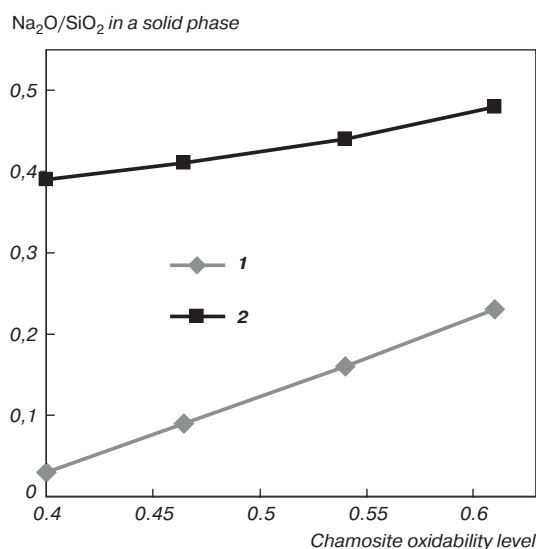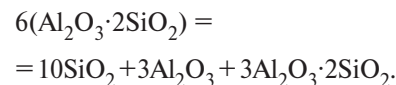

Fig. 6. Results of the experimental activity estimation of both natural and thermoactivated chamosite samples according to the SHA formation rate in a standard hydrochemical process:
1 — natural chamosite; *2* — chamosite after treatment at the temperature of 600 °C

a process. The experimental study has shown the possibility to reach an $(\mu_{si})_{act}$ value at the level of 8−10 units given the following stoichiometry of equation (2), corresponding the mullitization degree of 50%:

$$6(Al_2O_3 \cdot 2SiO_2) =$$
$$= 10SiO_2 + 3Al_2O_3 + 3Al_2O_3 \cdot 2SiO_2.$$

Among close kaolin analogues there are minerals of the peach group, widely represented in the content of a series of bauxite deposits and which behaviour in engineering processes is studied to essentially lesser degree. This leads to their unavoidable involving into manufacturing. Domestic factory practice unambiguously demonstrates significant difficulties, occurring on processing such a raw material in the course of the realized alumina production technology, which are connected with reduced extraction of aluminium oxide, low red mud thickening rate and problems of its utilization in ferrous metallurgy [11]. This stipulated the necessity to solve a complex of the questions, connected with the efficiency enhancement of working up the bauxites, containing minerals of kaolin and peach group and their analogues. Whereas there are certain well-established approaches to efficient kaolin processing as a part of bauxite raw material, such a clarity is lacking as applied to minerals of the peach group, and corresponding approaches deserve further considerations [4, 7, 8, 12].

Since minerals of the peach group are predominantly represented in home bauxites by sole mineral kind — chamosite, than it is the behaviour of this mineral that is worthy of the most notice. For investigation purpose there were selected six samples of the Kursk magnetic anomaly chamosite, which represents the most pure sort of this mineral according to the results of phase investigations by the means of *X*-ray diffractometry and crystallooptic analysis. At the same time, the samples contains insignificant amount of accompanying minerals (kaolin, haematite and siderite), genetically connected with chamosite formation on generating the residual soil under the influence of exogenous factors, causing the destruction of igneous rocks. An approximate chamosite composition may be represented by the following formula: $(Fe^{2+}, Fe^{3+})_3 \cdot [AlSi_3O_{10}] \cdot (OH)_2 \cdot \{(Fe, Mg)_3 (O, OH)_6\}$, which allows one to suggest an inconstancy of its chemical composition and separation of a series of minerals of the chamosite group. Chemical composition of the studied probes is listed in Table 1, which in full measure confirms the natural chamosite composition inconstancy

The reported results strongly support the availability of essential quality augmentation of the kaolin thermochemical processing products along with obtaining the concentrates, characteristics of which are acceptable for alumina production. At this, an optimization of the thermal and hydrochemical treatment conditions is an indispensable condition for achieving the high showings for such
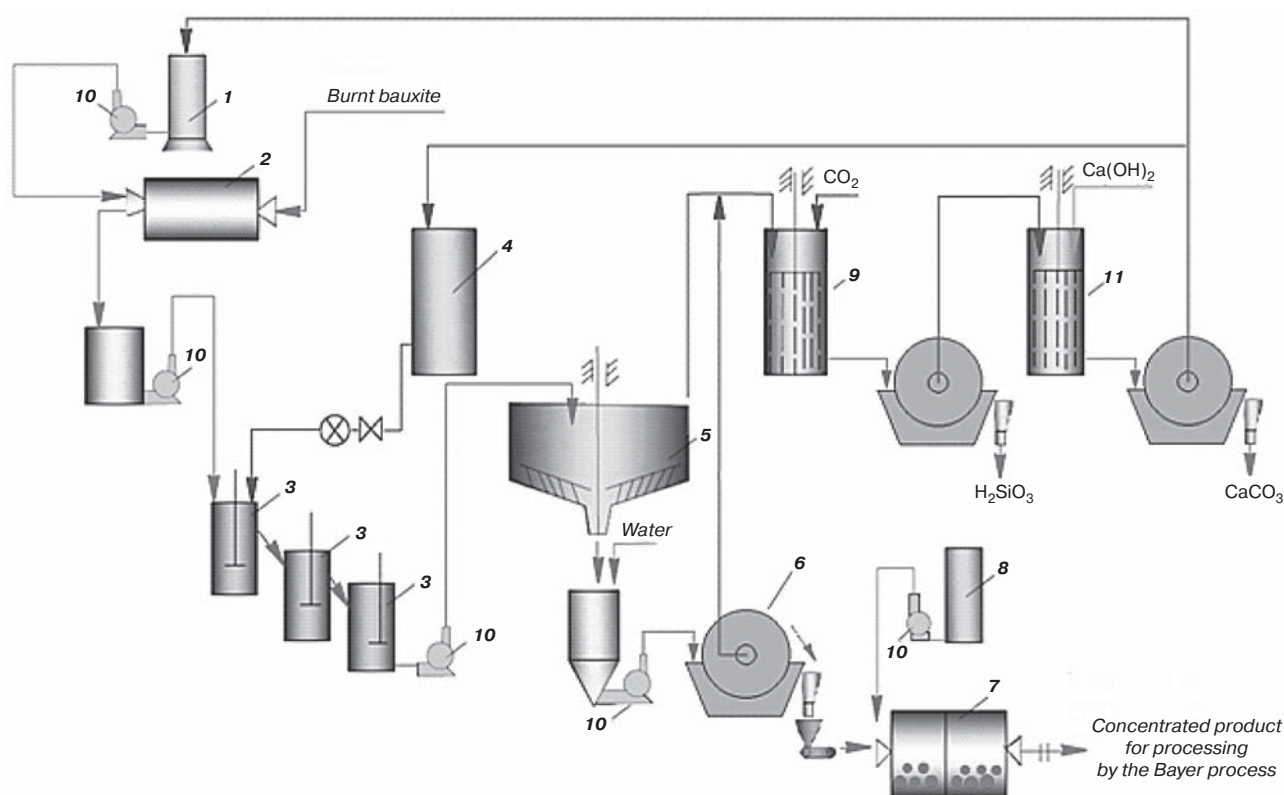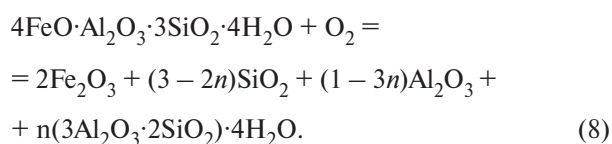
Fig. 7. Apparatus and process flowsheet of desiliconizing the low-grade bauxite raw material and its analogues:
1, 4 — tank of recirculated alkaline solution; *2* — rod mill; *3* — cascade of repulpers; *5* — thickener; *6* — drum vacuum filter; *7* — two-cell ball mill; *8* — tank of recirculated aluminate solution; *9* — carbonizer; *10* — pumps; *11* — causticizer

with respect to contents of crystalline modifications and iron with various oxidability levels.

Fig. 4 illustrates the results of the chamosite sample thermal study in an oxygen-free medium when heating the sample at the rate of 10 degrees per minute. At a DTG curve there has been fixed four calorific effects, among which the two ones have been accompanied by significant mass loss; the first one may be bound with elimination of adsorption water as mass changes by 4.70%. The second endothermic effect, characterized by the loss of constitution water (mass change is 1.61%), is fixed in a 233÷338 °C temperature range. In a temperature range from 338 to 1200 °C there are observed moderate endo- and exothermic effects concerned with dehydroxylation process and accompanied by loss of 5.74% of the mass. On heating above 1077 °C there are observed endo- and exothermic effects (mass change is 0.32%), mainly associated with the haematite and quartz crystallization process, which is confirmed by the results of *X*-ray phase analysis. This permits to suppose the following simplified stoichiometry of the chamosite thermal decomposition process for various product mullitization degrees:

$$4FeO \cdot Al_2O_3 \cdot 3SiO_2 \cdot 4H_2O + O_2 =$$
$$= 2Fe_2O_3 + (3 - 2n)SiO_2 + (1 - 3n)Al_2O_3 +$$
$$+ n(3Al_2O_3 \cdot 2SiO_2) \cdot 4H_2O. \qquad (8)$$

Then thermochemical chamosite transformations may be illustrated by the diagram in Fig. 5. Taking into account stoichiometry (8) and by analogy with equations (6—7), the design equations for determining silicon module of chamosite thermochemical processing products take the form (9—10), and calculations implemented by these equations also confirm the availability of appreciable quality improvement for chamosite processing products and rise of their silicon module with respect to initial value of 0.57 U:

$$(\mu_{si})_{act}^{ch} = 0.85(1 - 3n)/(3 - 2n)(1 - \varepsilon_{SiO_2}), \qquad (9)$$

$$(\mu_{si})_{gross}^{ch} = 0.85/[(1.5 - \varepsilon_{SiO_2}(1.5 - n)]. \qquad (10)$$

The activity assessment of chamosite thermal treatment products has been implemented on the base of their behaviour in a standard chemical process, including alkaline processing at 95 °C, which leads to formation of synthetical sodium hydroaluminate (SHA) with $Na_2O \cdot Al_2O_3 \cdot 2,4SiO_2$ stoichiometry. Then depending on the activity of thermal decomposition products, one can expect the Na_2O/SiO_2 ratio change in solid products from minimum values given low activity of components regarding SHA formation until maximum values, mee-

ting its stoichiometry at Na$_2$O/SiO$_2$ = 0.42. In Fig. 6 depicted are the results of the standard alkaline processing of four chamosite samples with different oxidability level in initial state and after thermal at a temperature of 600 °C. These results strongly show low chemical activity of natural chamosite regarding SHA formation under the stated conditions and considerable activity of the same samples after thermal treatment. At the same time, one can establish a noticeable influence of such a mineralogical characteristic as an iron oxidability level on chamosite activity.

The implemented analysis and experimental study allow one to suggest an essential rise of activity of hydrated aluminosilicates by the example of minerals of kaolin and chamosite series on thermal treatment in a temperature range of 600÷900 °C, which is accompanied by formation of amorphous forms of aluminium oxide and silicon. This permits to suppose the following apparatus and process flowsheet (Fig. 7) for realization of the considered engineering processes, possessing the required adaptation to the existing manufacturing methods of alumina production by alkaline methods.

Conclusion

1. Activation processes of minerals of kaolin and chamosite rows are based on their thermodynamic unsteadiness with reference to thermal dissociation with formation of amorphous silicon oxide and aluminium as primary products followed by generation of mullite and crystalline modifications of oxides as thermodynamically steady final products.

2. The multistage nature of kaolin and chamosite thermal decomposition processes allows to provide a difference in chemical activity of the products of their heat treatment, which create the necessary prerequisites for selective silica extraction into solution and rising silicon module of the products up to the values, acceptable for alumina production by alkaline methods.

3. The substantial selectivity factors of engineering process with respect to silicon and aliminuim are the mature of minerals, temperature and duration of heat treatment, resulting in differences in mullitization degree of the products, as well as indices of silica chemical extraction on hydrochemical treatment of activated materials.

References

1. State report on the condition and usage of mineral resources of the Russian Federation in 2013. Moscow : OOO "Mineral-Info", 2014. 387 p.

2. Arsentyev V. A., Gerasimov A. M., Mezenin A. O. Kaolines beneficiation technology study with application of hydrothermal modification. *Obogashchenie Rud*. 2017. No. 2. pp. 3–9. DOI: 10.17580/or.2017.02.01.

3. Brykov A., Krasnobaeva S., Mokeev M. Hydration of Portland Cement in the Presence of Highly Reactive Metakaolin. *Materials Sciences and Applications*. 2015. Vol. 6. pp. 391–400.

4. Wang Y., Xing S., Zhang Y., Li Z. Mineralogical and thermal characteristics of low-grade Jinlong bauxite sourced from Guangxi Province, China. *Journal of Thermal Analysis and Calorimetry*. 2015. pp. 917–927.

5. Gasafi E., Scarsella A., Hartman V., Schmidt H. W. The processing of high quartz bauxite. *Light Metals*. 2013. pp. 217–221.

6. Zimu Z., Shuchan W., Qiuyue Z. Economic Analysis of Producing Alumina with Low-Grade Bauxite (Red Mud) by Calcification-Carbonization Method. *Light Metals*. 2014. pp. 165–168.

7. Zhonglin Y., Guobao W., Liqiang Z., Xiaotao L. Progress in Research and Development of Alumina Production Technology for Low Grade Bauxite in China. *The 35th International ICSOBA Conference : proceedings*. Hamburg, 2017. pp. 289–299.

8. Yue Q., Wang H. M., Gao C. K. Resources saving and emissions reduction of the aluminum industry in China. *Resources Conservation and Recycling*. 2015. No. 104. pp. 68–75.

9. Bergaya F., Lagaly G. Handbook of clay science. 2nd edition. Amsterdam : Elsevier, 2013. 274 p.

10. Brichkin V. N., Vasilyev V. V., Nagornaya E. A., Gumenyuk A. M. Bauxite grade improvement through selective grinding. *Obogashchenie Rud*. 2017. No. 3. pp. 3–9. DOI: 10.17580/or.2017.03.01.

11. Sizyakov V. M., Dubovikov O. A., Nikolaeva N. V., Yakovlev M. G. Preparation of bauxites for the research of processing possibility of red slimes for their usage in ferrous metallurgy. *Tsvetnye Metally*. 2013. No. 2. pp. 57–62.

12. Sizyakov V. M., Dubovikov O. A., Loginov D. A. Lower grade bauxite thermochemical processing theory and practice. *Obogashchenie Rud*. 2014. No. 5. pp. 10–17.