



THERMAL AND DEFORMATIVE CHARACTERISTICS OF KAOLIN RAW DEPOSITS OF THE REPUBLIC OF BELARUS

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Abstract. The article gives brief information about the most common kaolin raw deposits of the Republic of Belarus. Thermal and dilatometric characteristics of natural kaolins and kaolins enriched by clarification method of “Sitnitsa” and “Dedovka” deposits are studied in detail. It is found that these raw materials are industrially prospective in terms of its using in the production of silica-alumina refractories (semiacid and chamotte).

Keywords: kaolin, differential thermal analysis, dilatometric curve, shrinkage, enrichment, refractories.

Introduction

Kaolin deposits of the Republic of Belarus differ from traditional kaolin in their structure and properties because of the significant amount of mechanical impurities, increased content of coloring matter and other impurities (Sergieievich *et al.* 2012). There are several kaolin deposits and occurrences on the territory of the Republic of Belarus, but the most common and studied are “Sitnitsa” and “Dedovka”.

Reserves of primary raw kaolin of “Sitnitsa” deposit are counted in the amount of 2.53 million tons of C₁ and C₂ categories with the expected output of enriched kaolin – 30.5%. The mineral is a gray clay rock, weakly chloritized with large inclusions of fragments mainly of feldspar-quartz composition, biotite, grains of quartz and feldspar. “Dedovka” deposit is represented by primary and secondary kaolins. It’s a rock of yellowish-gray color with mechanical impurities of glauconite-quartz sand, muscovite, feldspar and fragments of crystalline rocks. Total reserves of

primary raw kaolin are up to 7.02 million tons, the secondary – 1.23 million tons with a yield of enriched kaolin 48.8% versus 28.4% in the primary (Khomich *et al.* 2002).

Nowadays, refractory industry uses refractory clay and kaolin: primary, secondary, carried by water currents for the production of chamotte refractory and semiacid aluminosilicate products. In the absence of the companies and lines producing refractory products in the Republic of Belarus nearly 16.5 tons of fireclay refractory materials totaling 6.4 million \$ per year are imported into the country annually and consumed, 30–50% of which could be obtained on the basis of local raw kaolins.

The results of the research of some structural features and properties of primary kaolin deposits of the Republic of Belarus are known (Levitsky *et al.* 1995; 2008). The prospect of their industrial use in natural and enriched form in some industries of ceramic production, including refractory, can be installed at the

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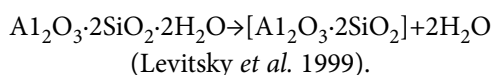
result of more deep and detailed study of characteristics properties of kaolins such as thermomechanical and deformation.

1. Experimental part

The average representative samples of primary kaolin "Sitnitsa" and "Dedovka" are used for research.

Phase transformations of the kaolin in the temperature range of 20–1200 °C were studied by differential thermal analysis, which was conducted by derivatograph DSC 404 F3 by the company NETZCH (Germany). Derivatograms of natural kaolins and kaolins, enriched by wet elutriation on the sieve number 0063 of deposits "Sitnitsa" and "Dedovka" are shown in Figure 1.

The presence of endothermic effect on DSC curves of kaolin "Sitnitsa" in natural form (Fig. 1a) at temperatures of 27–110 °C and 110–145 °C accompanied by removal of hygroscopic and adsorption water. A weight loss, corresponding to the first endothermic effect is 0.57%, to the second – 0.13%. Endothermic effect at temperatures near 150 °C on the curve of kaolinite is explained by presence of impurities of halloysite which has a composition similar to kaolinite ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$) (Brigatti *et al.* 2006). Intensive endothermic effect at temperatures 415–632 °C, accompanied by weight loss of 4.81%, corresponds to the destruction of the lattice of kaolinite upon cleavage and removing of crystallization water as the result of kaolinite decomposition according to reaction:

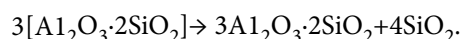


The metakaolinite [$\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$] – is amorphous product with partial kaolinite structure. In this case, kaolinite, devoid of chemically bound water, irreversibly loses plasticity. The observed splitting of endothermic effects as a small step in the DSC curve at a temperature of 570–580 °C is associated with transition of quartz from β - to α -form with the change in volume.

Exothermic effect in the temperature range of 978–1030 °C is associated with the processes of mullitization. In this case, there is dissociation of metakaolinite and subsequent merges of homogeneous structural units [SiO_4] and [AlO_4] in a more or less extended amorphous grouping of substances and the simultaneous growth of equivalence within the tetrahedral bonds. In parallel, sometimes a small amount of γ - Al_2O_3 or mullitlike phase is crystallized. There is

no clear argument for exothermic effect at 950–980 °C. It is most likely that the source of exothermic energy is a free energy of metakaolinite. Carbonates are dissociated with evolution of carbon dioxide, sulfides are oxidized to form sulfur dioxide and organic impurities are burn at temperature range of 700–1000 °C. These processes are accompanied by a weight loss of 0.67%, a slight increase in porosity and decrease in volume. General weight loss is about 6.20%.

Metakaolinite rearranges to form of mullite at temperature of 1100 °C with heat release according to reaction:



The amount of mullite continuously increases with increase of temperature, and reaches a maximum at a temperature of 1250–1350 °C. Prolonged exposure at temperatures above 1200 °C does not affect to the increase in the yield of mullite, but it promotes the growth of crystals. Theoretically, all the alumina contained in kaolin, should go into mullite, however, a practical way of mullite never reaches the theoretical one (Castelein *et al.* 2001). Division of mullite in origin during firing of kaolinitcomprising masses into primary and secondary, as well as the selection of cubic intermediate phase (aluminumsilicate spinel) is given in the work (Pavlov, Mitrokhin 1979).

The nature of thermal effects of the raw kaolin of "Dedovka" deposit (Fig. 1b) – is similar to kaolin "Sitnitsa". The first endothermic effect in the temperature range of 27–110 °C with a weight loss of 0.10% is characterized by a single minimum; the second endothermic effect is shifted right to 5–38 °C with a minimum at ~530 °C with a weight loss of 2.84%. Exothermic peak in the range of 960–1050 °C with a maximum at 988 °C is characterized by a somewhat larger area due to more active mullitization of kaolinite. It is characterized by a weight loss of 0.27%. The general weight loss is amounted to 3.21%.

When "Sitnitsa" and "Dedovka" kaolins are heated in enriched form all endo- and exothermic effects are expressed more deeply, compared to the natural ones because of the absence of impurity minerals, i.e. their derivatograms are close to the curves of traditional kaolinite. Thus there is no splitting effect as a step on a DSC curve at a temperature of 570–580 °C (Fig. 1a, b) connected with polymorphic transformations of impurity quartz. The presence of more deeply expressed endothermic effect on the curves of the enriched kaolins in this temperature range is determined only by

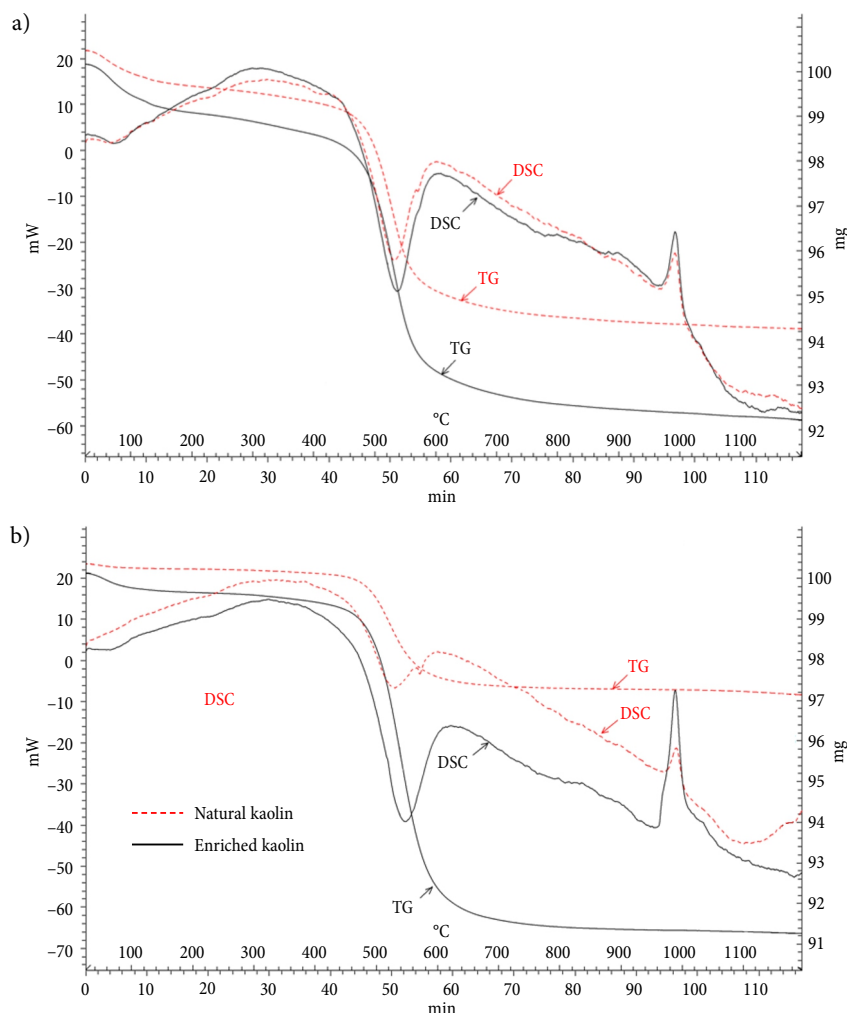


Fig. 1. Derivation of kaolin deposits "Sitnitsa" (a) and "Dedovka" (b)

the dehydration of the mineral and by the formation of the metakaolinite with the lattice ordered only in two directions. The exothermic effect undergoes a significant changes at temperature of 950–990 °C for enriched kaolins, which expands in this temperature range and is expressed by more intensely because of activation of the processes of restructuring prior to the formation of mullite (kaolinite mullitization) with decreasing volume.

It should be noted that if the Belarusian kaolin deposits contain impurities with temperatures of thermal effects, close enough to kaolinite, they are difficult to distinguish on the thermogram due to the high intensity of the thermal effects of the main mineral – kaolinite.

Figure 2 shows the high-temperature dilatometric curves of natural and enriched kaolin of "Sitnitsa" and "Dedovka" deposits in the temperature range of 100–1400 °C at a heating rate of 50 °C/min, obtained by optical heating microscope "MISURA ODHTSM 1600-80".

There is little change in the size of both the samples of kaolin at temperatures up to 500 °C, because their thermal expansion is largely compensated by shrinkage associated with the removal of the adsorbed water and the beginning of the dehydration of kaolinite. At a temperature of 500 °C expansion reaches its maximum value for the samples of enriched kaolin and goes into shrinkage which continues until the temperature of 735 °C for kaolin "Sitnitsa" and is 1.18% and up to 700 °C for kaolin "Dedovka" with shrinkage of 0.31% that is connected with removal of water of crystallization and the destruction of kaolinite lattice.

In this temperature range for both natural kaolin deposits is observed a slight expansion of the samples: 0.75% for kaolin "Sitnitsa" and 0.50% for kaolin "Dedovka". Probably it is connected with the polymorphic transformation of the impurity of quartz with an increase in volume.

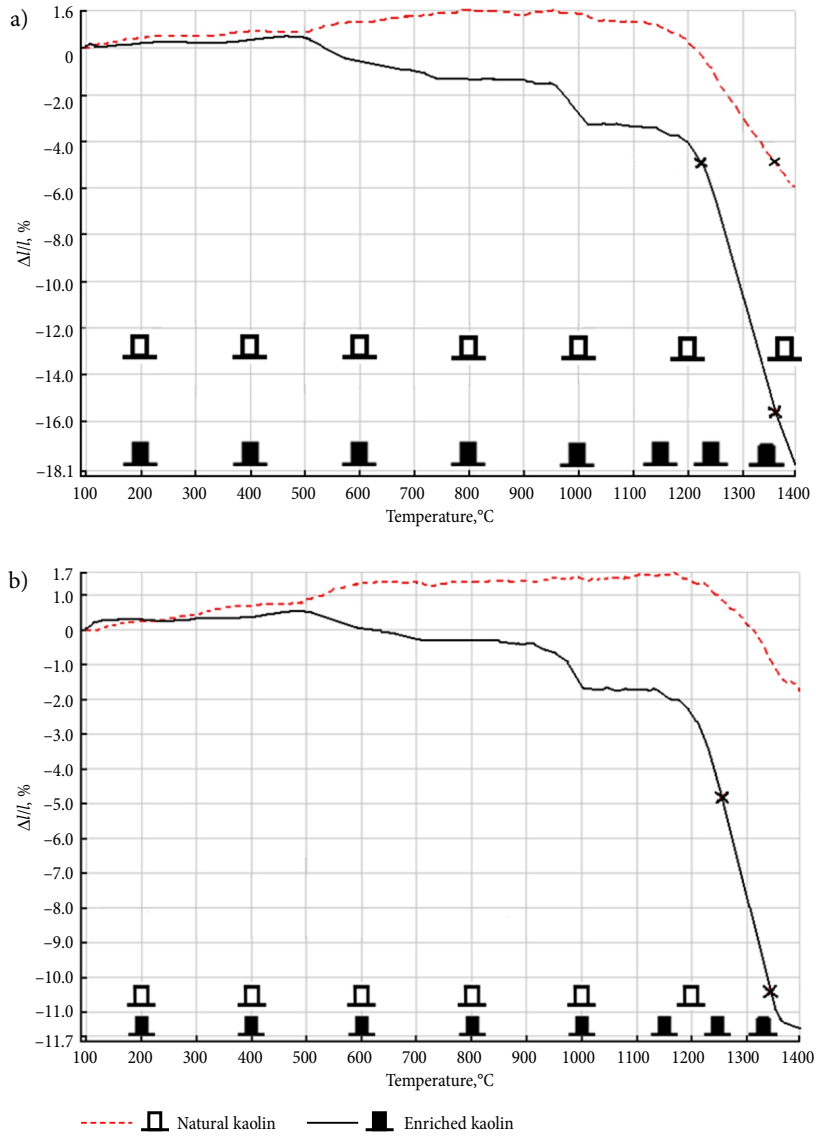


Fig. 2. The dilatometric curves of kaolin of “Sitnitsa” (a) and “Dedovka” (b) deposits

Further, up to a temperature of 945 °C, the sample size is almost unchanged: shrinkage is compensated by thermal expansion. The sharp shrinkage in the temperature range of 950–1050 °C for samples of enriched kaolin (2.08% – “Sitnitsa” and 1.44% – “Dedovka”) is determined by the dissociation of carbonate impurities, which present in small quantities, as well as beginning of the process of the mullite formation assists in sealing of structure.

Under these conditions unenriched kaolin samples, change their sizes with minor extension, which is likely determined by the formation of the modification phase of silica at 1060 °C – metastable α -cristobalite, a sharp increase in the volume of which is somewhat offset by combining structural units of metakaolinite. Above the temperature of 1150 °C there is a sharp

transition of dilatometric curves towards shrinkage, which indicates activation of the sintering process of kaolin both of deposits with the formation of mullite.

We should note the presence of the following thermal characteristic points on the dilatometric curve of enriched kaolin (the change of shape the sample in accordance with the procedure of study): 1) sintering, whereby sizing is set at 5% (the value of this temperature is 1225 °C for “Sitnitsa” kaolin and 1257 °C for “Dedovka” kaolin); 2) softening due to the liquid phase, which causes the rounding of corners and decrease of surface roughness, which corresponds to a temperature of 1362 °C for “Sitnitsa” kaolin with a total shrinkage of 15.70% and 1343 °C for “Dedovka” kaolin with a total shrinkage 10.45%.

Table 1. Chemical and technological parameters of raw kaolin

Indicator	“Sitnitsa” kaolin		“Dedovka” kaolin	
	natural	enriched	natural	enriched
Content of the defined component, %*:				
SiO ₂	61.7	46.1	70.3	50.7
Al ₂ O ₃ +TiO ₂	25.78	35.54	19.26	34.03
Fe ₂ O ₃	1.56	2.53	0.46	1.05
Content of fine fractions,%:				
<0.01 mm	27.6	81.4	17.0	55.1
<0.001 mm	11.7	48.9	7.5	26.0
Refractoriness, °C	1620	1710	1750	1780

Notes:*here and hereafter given weight content.

On the dilatometric curves of unenriched kaolin in the investigated temperature range temperature of the characteristic point of the sintering beginning is much higher: it is 1361 °C for natural “Sitnitsa” kaolin, and for “Dedovka” kaolin this point goes beyond the heating unit of measurement that indicates its higher fire resistance. Other characteristic points on the dilatometric curves of natural kaolin differences are not available, that is connected with their greater sanding, which prevents liquid phase sintering. Thus “Dedovka” kaolin has lower shrinkage values as compared with samples of “Sitnitsa” kaolin, that can also be explained by the presence of larger amounts of quartz impurities in the kaolin.

Table 1 summarizes the chemical and technological properties of the raw kaolin, characterized by the possibility of their use in the manufacture of refractory aluminosilicate as a main component of the mass.

It can be concluded that the content of Al₂O₃ in natural kaolin of the Republic of Belarus does not allow to use it for fireclay refractories (28–45%); it is necessary to add components with high content of Al₂O₃. Initial raw materials requirements according to general classification criteria (standard technical documentation) are satisfied for kaolin in the enriched form.

Conclusions

Phase transformations during heating of natural kaolin of “Sitnitsa” and “Dedovka” deposits are almost identical. It should be noted that the presence of impurities is difficult to discern on the derivatograms due to the high intensity of thermoeffect of the main mineral kaolinite.

Kaolin of Belarus deposits as traditional kaolinite gives dilatometric curves that fix sharp shrinkage at temperatures of return of crystallization water and the

beginning of kaolinite mullitization, which in turn can facilitate the selection of the firing (Lamberov *et al.* 2012).

It is established that in the production of aluminosilicate refractories both natural and enriched kaolin can be used, wherein the refractory industry has wide experience of mass production of such products obtained by dry pressing. By using unenriched kaolin raw materials low alumina semiacid aluminosilicate refractory materials can be obtained and on the basis of enriched kaolin – fireclay sealed aluminosilicate refractory materials in accordance with standard technical documentation.

High sanding of kaolin of the deposits of the Republic of Belarus allows using of feldspathic sands formed during their conditioning in the amount of 65–70%, and the natural raw materials in the production of ceramic bricks with high thermomechanical characteristics used for masonry residential furnaces, heating units etc.

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