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Analysis of some properties of model system from low-melting illite clay and fibrous mineral wool waste

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In recent years, recycling of fibrous mineral wool waste has become an acute problem. The present paper addresses this problem by suggesting a promising technique based on using fibrous mineral wool waste and low-melting illite clay with appropriate additives. The results obtained have shown that by applying an adequate calculation method it is possible to predict the fusibility characteristics of a selected chemical composition. The SiO_2–CaO–Na_2O system with the oxides Al_2O_3, MgO and Fe_2O_3 influencing its fusibility is considered. Fusibility characteristics of the investigated systems have been calculated and their structural changes were analysed.

Key words: *low-melting illite clay; fibrous mineral wool waste; fusibility characteristics*

1. Introduction

In recent years, recycling of waste materials has become an acute problem [1–4]. In manufacturing mineral wool, large amounts of waste materials are obtained. The waste consists of mineral wool fibres, pieces of unopened fibres (beads) and a small amount of organic binder (1–2%). Recycling of mineral wool waste is an important problem. When a melt used in mineral wool manufacture is obtained in bath furnaces, mineral wool waste may be remelted. However, when a cupola furnace is used, this is hardly possible because these furnaces are intended for melting lump raw materials. Therefore, small fibres of the waste clog up the feeding equipment of air and oxygen.

Jensen offered a briquetting technique to be used to charge cupola furnaces with briquettes and coke [5]. Miankovski described briquetting technology of basalt waste [6]. Some efforts were made to use briquetting for recycling mineral wool waste. Holdbek took out a patent for technology based on binding waste materials with Port-

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land cement which is a hydraulic binder [7]. However, in melting the briquettes bound with Portland cement under high temperature, they split into small pieces before starting to melt, thereby making remelting in the cupola furnace impossible because of the broken feeding of air and gases [8].

In addition to Portland cement, some other binding materials may be used for waste material binding. Nefedova offered a technique based on binding waste materials with liquid glass [9]. However, this method has a drawback because in this case only beads may be used. The tests performed show that a promising mineral wool recycling technique is the use of low-melting illite clays [8, 10].

The main parameters considered in evaluating the silicate melt obtained in various furnaces are fusibility characteristics of the charge. It is well known that these characteristics can be determined by a theoretical approach which is extensively used in selecting the composition of various silicate glass charges [11]. To calculate technological parameters of various kinds of glass viscosity constant and additiveness, the formulas describing the viscosity characteristics of the Na_2O–CaO–SiO_2 glass with the additives MgO and Al_2O_3 are used. Having in mind that the compositions of low -melting illite clay and fibrous mineral wool system are close to that of silicate glass, the above theoretical method of determining fusibility characteristics can be applied to choose the composition of the investigated system consisting of low-melting illite clay and fibrous mineral wool waste. This is of particular importance for selecting the composition of the system under investigation as well as some additives and determining the effect of additives on the system fusibility.

The present paper aims to study the composition of fibrous mineral wool waste and low-melting illite clay and to determine theoretically the fusibility characteristics and the effect of some additives on relevant characteristics.

2. Experimental

Chemical compositions of the tested raw materials, i.e. low-melting illite clay, fibrous mineral wool waste, cement dust, dolomite and basalt, are given in Table 1.

Table 1. Chemical compositions of raw materials used in testing

Substance	Chemical composition, %						
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	$Na_2O + K_2O$	Loss on ignition
Low-melting illite clay	46.00	15.80	5.20	8.20	3.70	5.00	1.00
Cement dust	13.50	3.50	2.50	45.00	2.50	4.20	28.00
Mineral wool waste	46.00	14.50	10.00	18.60	9.10	1.50	0.00
Dolomite	3.80	1.20	0.00	28.40	19.80	0.00	46.80
Basalt	48.30	17.60	11.20	11.00	7.80	3.40	0.70

A model system of low-melting illite clay – fibrous mineral wool waste was used. The additives of dolomite or cement dust were also introduced. Four series of specimens were prepared for testing. The compositions of specimens were as follows: series S1 – 35% clay, 15% dolomite, 50% fibrous mineral wool waste; series S2 – 35% clay, 10% dolomite, 5% cement dust, 50% fibrous mineral wool waste; series S3 – 30% clay, 15% dolomite, 5% cement dust 50% fibrous mineral wool waste; series S4 – 66% clay, 17% cement dust, 17% fibrous mineral wool waste.

In testing, cement dust obtained from a joint-stock company 'Akmenės cementas' was used. Cement dust is a finely divided mineral material made up of the components of various compositions and origin. Non-calcined cement dust consists of calcite, mica, quartz and dolomite. Chemical compositions of test specimens are presented in Table 2.

Table 2. Chemical compositions of test specimens (without loss on ignition)

Specimen series	Chemical composition, %					
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	$Na_2O + K_2O$
Series one (S1)	44.97	12.23	7.58	19.81	11.00	2.13
Series two (S2)	45.13	12.26	7.66	20.57	9.94	2.34
Series three (S3)	43.32	11.94	7.48	21.81	10.84	2.19
Series four (S4)	47.23	10.99	6.21	21.23	7.15	3.59

Fusibility characteristics of test specimens have been calculated based on the relationship between their chemical compositions and additivities [11]. Temperatures (t_η) have been calculated at which the viscosity of the melt is 10^2 Pa·s, indicating a limiting fusibility value of the charge; 10^3 Pa·s is the value of fusibility characteristic of the beginning of fibre formation; 10^8 Pa·s is a limiting value, showing the lower bound of fibre formation.

The temperatures have been calculated from the following equations [10, 11]:

$$t_{\eta=10^2} = A_2x + B_2y + C_2z + D_2 \tag{1}$$

$t_{\eta=10^2}$ is the melting temperature (°C) at which the viscosity is 10^2 Pa·s; the constants in the equation are as follows: $A_2 = -22.87$, $B_2 = -16.10$, $C_2 = 6.50$, $D_2 = 1700.40$;

$$t_{\eta=10^3} = A_3x + B_3y + C_3z + D_3 \tag{2}$$

$t_{\eta=10^3}$ is the softening temperature of a specimen (°C), at which the viscosity is 10^3 Pa·s; a sample is deformed under its proper weight; $A_3 = -17.49$, $B_3 = -9.95$, $C_3 = 5.90$, $D_3 = 1381.40$;

$$t_{\eta=10^8} = A_8x + B_8y + C_8z + D_8 \tag{3}$$

$t_{\eta=10^8}$ is a softening temperature of a specimen (°C), at which viscosity is 10^8 Pa·s; a sample is deformed under the action of an external force; $A_8 = -9.19$, $B_8 = 1.57$, $C_8 = 5.34$, $D_8 = 762.50$. In all equations x is the amount of $Na_2O + K_2O$, %, y is the quantity of CaO + MgO, %, and z is the amount of Al_2O_3, %.

Structural changes are determined by X-ray difractometer Dron-2 with the following operational characteristics: copper cathode, nickel filter, anode (plate) voltage – 30 kV, anode (plate) current – 8 mA, goniometer slots – 0.5, 1.0 and 0.5 mm, the rotation of the goniometer meter – 2°/min. Phase composition was identified by using ASTM card index of reference data.

Differential thermal analysis (DTA) was made with a derivatograph Q-1500, in ambient atmosphere, at the rate of temperature variation amounting to 10 °C/min. The melting point of the samples and characteristic changes in their shape in calcining were determined with a high-temperature microscope MHO-2.

3. Results and discussion

One of the major fusibility characteristics of a silicate system determining physical and mechanical properties of the charge of mineral wool is the viscosity of a silicate melt. Fusibility of a charge is determined experimentally by melting the charge of a known chemical composition in a laboratory furnace, as well as forming mineral wool in a special centrifuge and assessing the fibre yield. The experimental methods are reliable, but very expensive (requiring long-term testing and special equipment). However, fusibility of the considered charge can be determined by using the appropriate technique. It is claimed in the literature surveying theoretical methods of determining the viscosity of a silicate system that the choice of a particular method depends on its constituent oxides [11]. By using a mathematical method for determining the viscosity of the investigated silicate system, it is possible to determine the effect of particular oxides on the viscosity of the whole system and, consequently, to modify its composition. In the present investigation, the SiO_2–CaO–R_2O system with the oxides Al_2O_3, MgO and Fe_2O_3 influencing the system fusibility is considered. Fusibility characteristics of the investigated system are calculated and its structural changes are analysed.

Sample composition was proportioned for mineral wool manufacture and was calculated, taking into account mineral wool acidity modulus R_m which could not be lower than 1.9, and viscosity modulus K_m, the value of which should be lower than 1.6. The composition with 50% of mineral wool waste was used to make specimens of S1, S2 and S3 series. However, specimens of S4 contained only 17% of mineral wool waste.

The variation of the melting point and softening temperature of specimens, depending on their composition, is presented in Table 3. The temperatures at which the viscosity of test specimens was 10^2 Pa·s, 10^3 Pa·s and 10^8 Pa·s were calculated.

Table 3. The results obtained in calculating fusibility characteristics of specimens

Specimen series	$t_{\eta=10^2}$, °C	$t_{\eta=10^3}$, °C	$t_{\eta=10^8}$, °C	$t_{\eta=10^3} - t_{\eta=10^8}$, °C
Series S1	1235	1112	857	255
Series S2	1235	1112	854	258
Series S3	1202	1091	857	234
Series S4	1233	1104	833	271
Charge: basalt 80%, dolomite 20%	1294	1153	811	324

As shown in Table 3, fusibility characteristics of the specimens of series S1 and S2 are similar. A comparative analysis of the data obtained for S1, S2 and S3 specimens has shown that softening temperature of specimen S3 decreased from 1112 °C to 1091 °C when the viscosity was 10^3 Pa·s, while its melting point decreased from 1235 °C to 1202 °C, when the viscosity was 10^2 Pa·s. It should be noted that the addition of 15% dolomite to specimen S3 considerably changes its fusibility. Thus, the calculated temperature at which the viscosity of the specimen was 10^2 Pa·s decreased to 1202 °C, however, the smallest temperature interval of 234 °C was observed for fibre formation (Table 3).

The analysis of theoretical data has shown that the largest temperature interval of fibre formation was obtained for S4 specimens. The study of the calculation results has revealed that the addition of dolomite negatively affects melting characteristics. This may be accounted for the highest value of the relationship between CaO and MgO in the investigation system of the fourth series compared to the respective values obtained for three other compositions, also characterized by a smaller amount of Fe_2O_3.

A comparative evaluation of the calculated characteristics of all four series of specimens and the calculated fusibility characteristics of the specimen consisting of 80% basalt and 20% dolomite was made (Table 3). The comparative analysis has shown that the values of fusibility characteristics of all four specimen series (S1, S2, S3 and S4) are lower than those of the basalt and dolomite specimen.

The experimental results in determining fusibility of specimens were obtained by using the high-temperature microscope MHO-2 (Fig. 1). Test specimens were heated in the temperature interval of 20–1250 °C and typical changes in their shape were determined. Testing a specimen of S1 series at the temperature amounting to 1160 °C no characteristic changes in its shape were observed. When the temperature was increased up to 1210 °C, a considerable contraction of the specimen could be seen, while melting of the specimen was observed at 1230 °C.

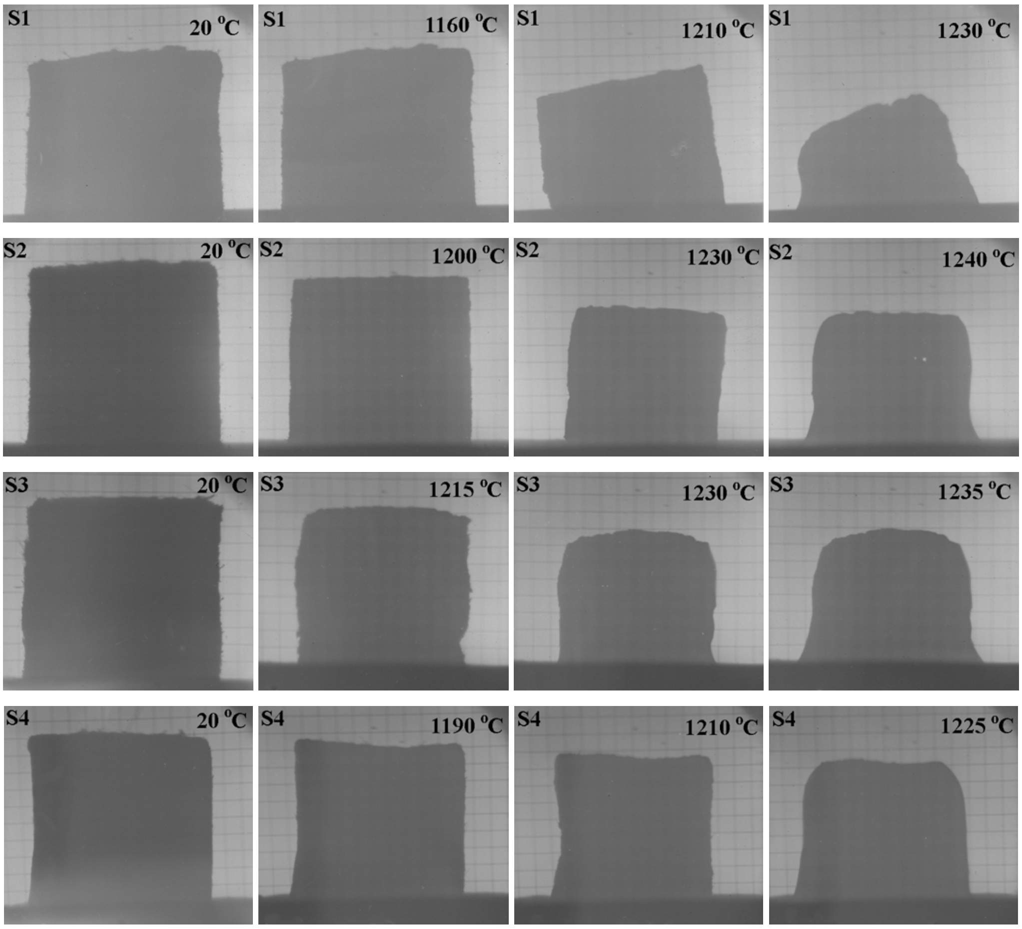

Fig. 1. The experimental results of determining fusibility of specimens S1–S4

When a portion of dolomite in the specimen S2 was substituted by cement dust, the character of the specimen contraction changed. A typical contraction could be observed at higher temperatures. In the temperature interval from 20 °C to 1200 °C the specimen did not change, while its contraction could be observed at a higher temperature (1230 °C). The melting point of the specimen also changed, increasing to 1240 °C. The analysis of the test results obtained for specimen S3 has shown that the increase of dolomite content in the specimen by 15% changes its fusibility. Characteristic changes in the specimen shape in heating, indicating the formation of a liquid phase, could be already seen at 1215 °C, while the observed contraction of the specimen was developing simultaneously with its melting. The melting point (1235 °C) of specimen S3 matches the test results of specimens S1 and S2.

The data obtained in differential thermal analysis (DTA) are presented in Fig 2. DTA curves are similar for all test specimens. They are characterized by exothermic effect in the temperature interval of 400–500 °C, demonstrating the burning of phenol–formaldehyde binder found in the mineral wool waste. In tested specimens S1, S2 and S3, endothermic effects were observed at 800 °C and at 850–860 °C. DTA curves show that the above effects indicate a decomposition of carbonates introduced into the specimens together with illite clay minerals, dolomite and cement dust. Endothermic effect observed at 800 °C demonstrated the decomposition of $MgCO_3$ found in dolomite, while endothermic effect observed at 850 °C and 860 °C showed the decomposition of $CaCO_3$ found in dolomite and cement dust. It should be noted that the most intense $CaCO_3$ bonds breakage was observed in the test specimen containing the largest amount of dolomite and cement dust, reaching 15% and 5%, respectively.

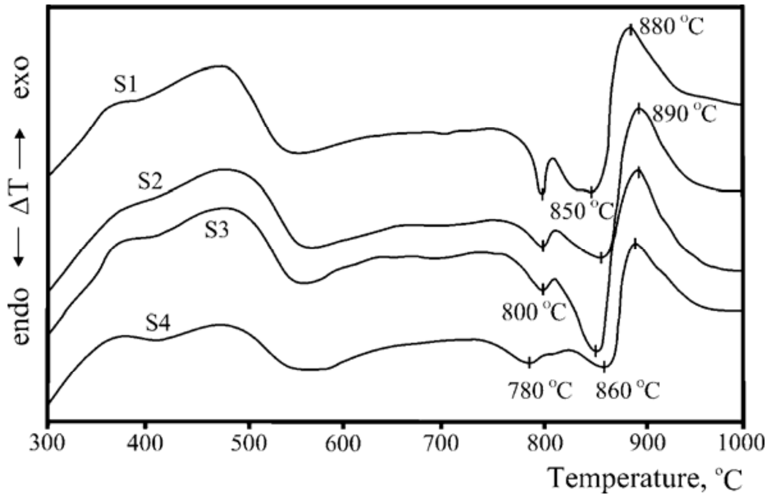

Fig. 2. DTA curves of specimens S1–S4

A comparative differential thermal analysis has revealed that decarbonization of low-melting clay takes place at a lower temperature in the case of specimen S4. This is shown by an endothermic effect observed at 780 °C. At the same time, decarbonization temperature of $CaCO_3$ did not change.

The crystallization of newly formed substances in heating test specimens was studied by the X-ray method (Fig. 3). The test specimens were heated up to 1000 °C. The results obtained show that fibrous mineral wool waste exothermal crystallization, taking place in the temperature interval of 820–850 °C, is accompanied by diopside formation (Figs. 2, 3). It was found that crystallization of mineral wool waste depends on the content of waste materials in the test specimens. The crystallization of the specimens S1, S2 and S3 containing 50% of mineral wool waste is accompanied by a clearly observed exothermic effect, while this effect is much weaker in the specimen S4 containing only 17% of mineral wool waste. A comparative X-ray analysis of the test data shows that after heating the specimens diopside spikes are less intense for specimens S4 than for specimens S1, S2 and S3. It should be noted that all test specimens have the composition not allowing the formation of the ion concentration gradient of Ca^{2+} and Mg^{2+}. Thus, ion diffusion of Ca^{2+} and Mg^{2+} in the mineral wool waste is inhibited. At the same time, the concentration of Na^{+} ions is low enough to allow them to distribute in the crystalline structure of the test specimens without forming any compounds.

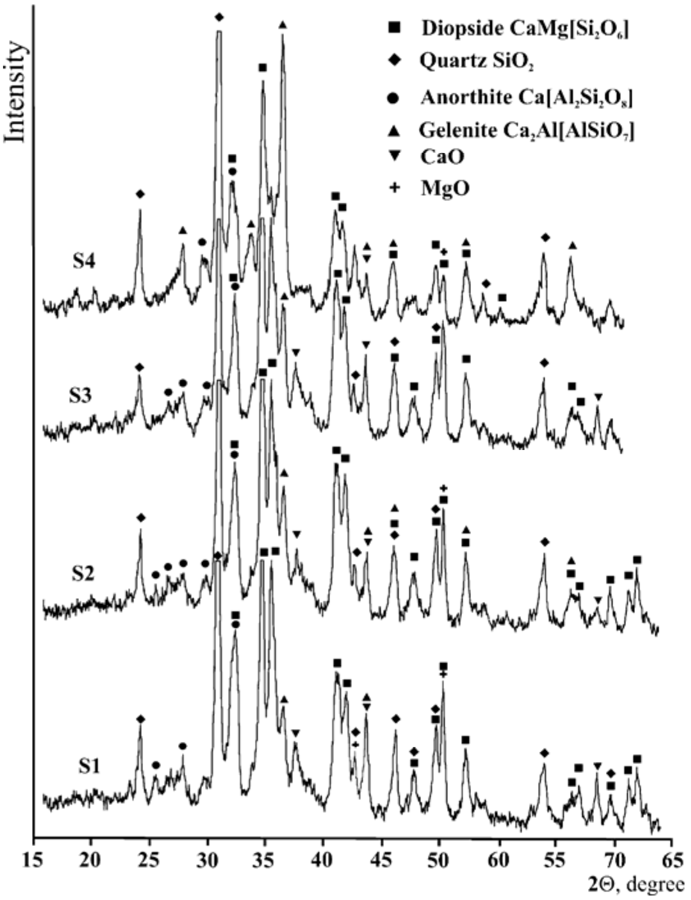

Fig. 3. X-ray diffraction patterns of specimens S1–S4

X-ray analysis of the data showed that the carbonates contained in the test specimens decarbonize without forming any compounds. The decarbonization of the carbonates contained in the test specimens which takes place between 800 °C and 860 °C causes the interaction between Ca^{2+}, Mg^{2+} ions and minerals of the illite clay. In the temperature interval of 880–900 °C crystallization of the exothermic reaction products was observed when the mineral anorthite and gelenite (of the plagioclase group) were crystallizing (Figs.2, 3). It should be noted that in the specimens S1, S2 and S3 containing 50% of fibrous mineral wool waste, a certain portion of carbonates formed in the decarbonization does not react with the illite clay minerals. Therefore, spikes of free CaO and MgO can be clearly seen. This may be attributed to low illite clay content (30–35%) in these specimens.

The tests have shown that to avoid the formation of free CaO and MgO, the smaller amount of dolomite should be used in specimens. The analysis of roentgenograms of gelenite spikes in specimen S4 has revealed that calcite $CaCO_3$ found in cement dust reacts violently with illite clay minerals. Therefore, relatively small amounts of free CaO and MgO can be found in specimens S4.

4. Conclusions

The analysis of the data presented in the paper shows that a model system based on low-melting illite clay, cement dust, dolomite and mineral wool waste is an effective way to solve the problem of fibrous mineral wool waste recycling. The experimental data proved the effectiveness of the suggested methods of calculating fusibility characteristics for determining of model system from low-melting illite clay and fibrous mineral wool waste. The above methods were successfully used in calculating fusibility of investigation model system. The results obtained also show that the calculated temperature values for specimens of all four series, when the viscosity is 10^2 Pa·s and 10^3 Pa·s, are lower than those practically used for the charge consisting of 80% basalt and 20% dolomite. It was found that the formation of free CaO and MgO in calcining could be avoided by reducing the content of dolomite.

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