The influence of mineralogical composition on the colour of clay body

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Abstract

By using methods of Mössbauer spectroscopy, X-ray diffraction and colorimetrics analysis, the dependence of the colour of a ceramic body on its mineralogical composition was determined. In order to achieve this objective, the mineralogical composition and colour parameters of the Girininkai deposit (Lithuania) easily fusible clay and its mixture with the glauconite rock during firing at 600, 800, 1000, and 1025 °C were investigated in detail. By changing firing temperature from 600 to 1025 °C and duration of isothermal exposure from 0.5 to 4 h the amount of iron in hematite increases 5 times, whereas the amount of Fe^{3+} incorporated into the crystal lattice of other compounds diminishes 3–4 times if compared with natural clay. For this reason, the value of red colour coordinate increases from 18.44 to 23.65 NBS units and the ceramic body darkens and becomes redish brown. The colour can be intensified even more by adding to the forming mass finely ground glauconite.
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1. Introduction

Following old architectural traditions, red ceramic bricks and tiles are widely used for the construction of dwelling and public buildings in Lithuania. Unfortunately, the colour of the facing bricks and roof tiles manufactured from the clay obtained from presently working deposits in our country is pale, pale red. It is very often inadmissible for consumers and especially restorers. Besides, most customers request products of other colours.

The colour of the ceramic body depends not only on the total iron amount in the mixture, but also on the way the iron is combined in clay minerals and additives and on what compounds, containing iron, are formed during the firing process of the ceramic body. During the firing of clay of different chemical composition different compounds are formed and this is the reason for a different colour of the ceramic body.[1,2] Iron oxides dye the ceramic body in red. The authors established that red tones become weaker when more iron incorporates in the structure of the compounds and less remains in the iron oxides.[1] Yellow or light brown colour of the ceramic body is

obtained when metakaolinite, mullite, pyroxenes or melilites are formed.[2] During the process of firing of the ceramic body iron can be integrated in the crystals lattice of other compound in such a way as making hard solutions. Some part of its ions may be changed into different (Mg^{2+}, Mn^{2+}) ions influencing magnetic features or paramagnetic compounds may be formed, containing not only iron, but also aluminum and silicon ions.[3] Therefore traditional methods for establishing the mineralogical composition (X-ray diffraction, simultaneous thermal analysis, IR spectoscopy) often provide insufficient information. It must be supplemented with Mössbauer spectroscopy data.[4–10]

The colour of a ceramic article can be changed with the help of various pigments,[11–20] waste products[21–26] or natural raw materials[11,12,27–30] containing a lot of colorific oxides. Lithuania is rich in natural rock glauconite (more than 1 billion tons), the chemical structure of which contains a lot of iron and alkaline metals. The latter should reduce the sintering temperature of the ceramics, and the colour of the ceramic body could be changed by iron compounds. Unfortunately, due to high mining expenses glauconite mines still are not used. They will pay to be used only when there is a big need of this raw material. Therefore, the possibility of using glauconite rocks from Merkys and Sventoji deposits (Lithuania) in ceramic production was investigated.[30,31] It was estimated that quartz,

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Table 1
Chemical composition of used materials, in wt.%.

Materials	SiO_2	$Al_2O_3 + TiO_2$	Fe_2O_3	CaO	MnO	MgO	Na_2O	K_2O	LOI
Clay from Girininkai	47.69	14.12	6.19	9.05	0.06	3.59	0.96	3.32	11.9
Sventosios glauconite rock	51.52	6.80	12.86	9.89	0.01	2.05	0.62	3.03	8.34

potassium–sodium feldspar and minerals of hydromica group (glauconite, muscovite, illite) prevail in these glauconite rocks. Glauconite rocks in molding mixtures behave as a nonplastic additive and slightly dyes the clay body.[30] Both glauconite rocks could be used in ceramics production, but obtained results proved that ceramic body made from Sventoji glauconite rock showed better physical mechanical properties than the ceramics produced from Merkys glauconite.[30,31] For this reason only the dependence of the colour of Sventoji glauconite rock on the change of its mineral composition during the firing process was investigated in this work.

To ensure the manufacture of a steady, acceptable for the customer production, it is necessary to investigate what compounds, formed during the firing process, determine the colour of Lithuanian clays ceramic body, how technological factors (mixture composition, firing regime) influence the formation of necessary compounds, and how the colour could be controlled by using glauconite additives.

The aim of this work was to investigate the influence of the change of a mineralogical composition of easily fusible clays and glauconite rock during the firing procces on the colour of a ceramic body and to evaluate suitability of glauconite rock for the colouring of the ceramic body.

2. Experimental method

Clay of the Girininkai pit (Lithuania) was dried at 105–110 °C, then it was grained by a dismembrator into grains smaller than 1 mm. The chemical composition of the clay is presented in Table 1.

Glauconite rock from Sventoji deposit was dried at 105–110 °C and used of natural fineness (specific surface area (S_a) – 50 m^2/kg) and ground in a porcelain ball mill ($S_a = 250 \pm 10$ and $350 \pm 10\,m^2$/kg). The chemical composition of Sventoji glauconite rock is presented in Table 1.

For the preparation of the samples, the amounts of dry powder of clay and additive were mixed for 1 h. Then the water was poured into mixtures for preparation of a plastic forming mixture with humidity of 20–24%. Slabs of the size 60 mm × 30 mm × 10 mm and samples of the size 120 mm × 15 mm × 15 mm were formed from these mixtures, dried at 105–110 °C and fired in laboratory furnace (with a temperature bias no larger than ±3 °C). Temperature was increased in two different regimes. In the first case, the temperature was increased up to 120 °C at 200 °C/h rate, afterwards, at 500 °C/h rate up to the desirable temperature. In the second case, the temperature was increased at the same rate, 200 °C/h. The firing temperature of the samples was 600, 800, 1000 and 1025 °C, while the duration of isothermal exposure at the desirable temperature was 0.5, 2, or 4 h.

Chemical composition of raw materials was determined by classical methods of chemical analysis, atomic adsorption spectrophotometer using adsorption and emission methods.

$^{57}_{26}$Fe Mössbauer spectra were collected at room temperature in a standart transmission geometry using a standart constant acceleration spectrometer with a $^{57}_{27}$Co(Rh) source. The velocity scale (±10 mm/s) was calibrated with referente to the magnetic sextet spectrum of a metallic iron foil absorber and all isomer shifts are given with respect to the centre of this spectrum. The spectra were analysed by decomposition into quadrupole doublets and sextets. Lines of Lorenzian shape were distinguished using least-squares program.

The X-ray powder diffraction (XRD) data were collected with DRON-6 powder X-ray diffractometer with Bragg–Brentano geometry using Ni-filtered Cu Kα radiation and graphite monochromator, operating with voltage 30 kV and emission current of 20 mA. The step-scan covered the angular range 5–60° (2θ) in steps of 2θ = 0.02°.

IR spectra were carried out with the help of spectrometer PerkinElmer FT-IR system Spectrum X. Specimens were prepared by mixing 1 mg of the sample in 200 mg of KBr. The spectral analysis was performed in the range of 4000–400 cm^{-1} with spectral resolution of 1 cm^{-1}.

In order to establish the dependence of the colour of a ceramic body on the changes of the mineral composition occurring during the firing process, the change of colour was measured by comparing the coordinates values of red a^* and yellow b^* colours and observing the change of lightness L^*. Colour measurements were made by using a spectrophotometer (SPECTRAFLASH SF450 X) and the results were expressed in L^*, a^*, b^* values. These parameters were measured for an illuminant D65, following the CIELab colorimetric method. In this system, L^* is the degree of lightness and darkness of the colour in relation to the scale extending from white ($L^* = 100$) to black ($L^* = 0$). a^* is the scale extending from green ($-a^*$) to red ($+a^*$) axis and b^* is the scale extending from blue ($-b^*$) to yellow ($+b^*$) axis. L^*, a^*, b^* values are measured in units of NBS (unit of the USA National Bureau of Standards and corresponds to one threshold of colour distinction power, i.e. the least difference in colour which the trained human eye can notice).

3. Results and discussion

By using methods of Mössbauer spectroscopy, X-ray diffraction and colorimetrics analysis, the dependence of the colour of a ceramic body on its mineralogical composition was determined. In order to achieve this objective, mineralogical composition, colour parameters and their changes of the Girininkai clay, glauconite rock of the Sventoji during firing for 0.5, 2 and 4 h at 600, 800, 1000, and 1025 °C were investigated in detail.
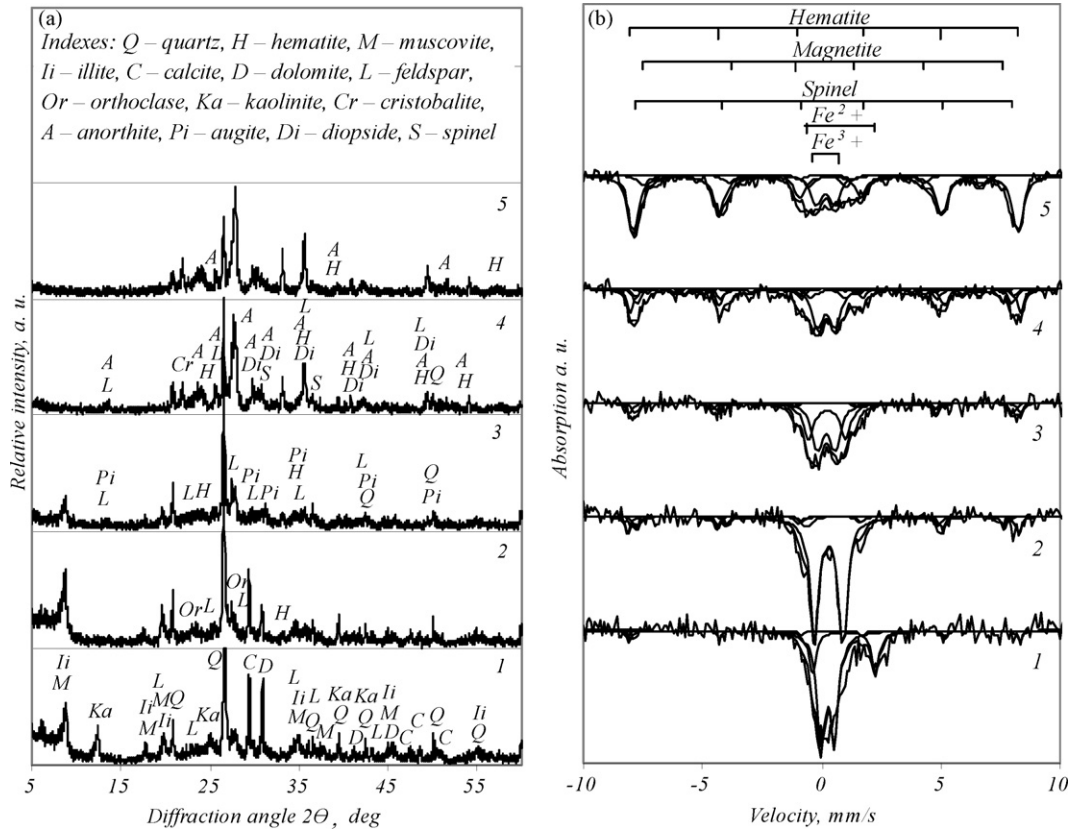
Fig. 1. X-ray diffraction paterns (a) and Mössbauer spectra (b) of Girininkai clay (1) and ceramic body from it, fired at 600 °C (2), 800 °C (3), 1000 °C (4), 1025 °C (5) for 4 h.

3.1. Girininkai clay

It is determined that the clay from Girininkai pit is hydromica clay. According to Fig. 1a (curve 1), illite (d – 1.300, 0.450, 0.333, 0.256, 0.199 nm) and muscovite (d – 1.100, 0.449, 0.336, 0.256 nm) minerals prevail in it, and there is also kaolinite (d – 0.710, 0.441, 0.356 nm) and a big amount of SiO_2, in the form of quartz sand (d – 0.425, 0.334, 0.246, 0.182 nm) as well. Calcite (d – 0.303, 0.228, 0.209, 0.191 nm), dolomite (d – 0.288, 0.219, 0.178 nm) and feldspar (d – 0.354, 0.348, 0.319 nm) are found among nonplastic admixtures.

There are two doublets in Mössbauer's spectrum of Girininkai clay (Fig. 1b, curve 1). One of them (IS = 1.033 mm/s, QS = 2.653 mm/s) is correspondent to Fe^{2+} that is in the structure of illite and muscovite crystal lattice.[4] Fe^{2+} makes 26% of total iron. Another, more intensive doublet (IS = 0.354 mm/s, QS = 0.555 mm/s), is attributed to Fe^{3+}. It predominates in Girininkai clay and comprises 65.03% of total iron (Fig. 2a, curve 1). Besides the abovementioned doublets, when the magnetic field is 517.3 kOe, a small intensity sextet (IS = 0.374 mm/s, Q = −0.316 mm/s) in Mössbauer's spectrum can be seen. The parameters of the sextet are very close to the
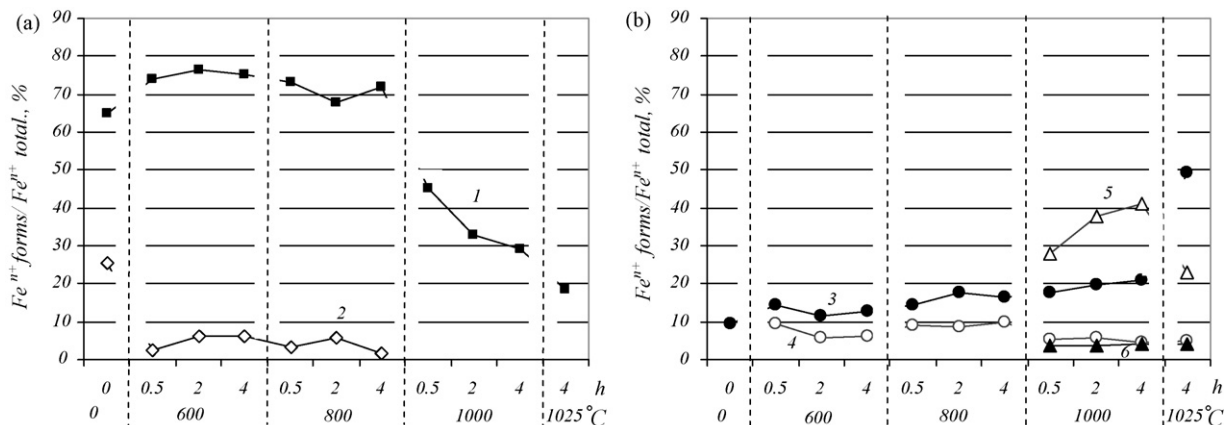

Fig. 2. Distribution of iron in the structure of compounds (a) and in oxides (b) in the clay body, depending on the firing temperature and on the duration of isothermal exposure. (1) Fe^{3+}, (2) Fe^{2+}, (3) Fe_2O_3, (4) Fe_3O_4, (5) $Mg(Al,Fe)_2O_4$, and (6) $Fe_{2-x}(Al,Si)_xO_3$.
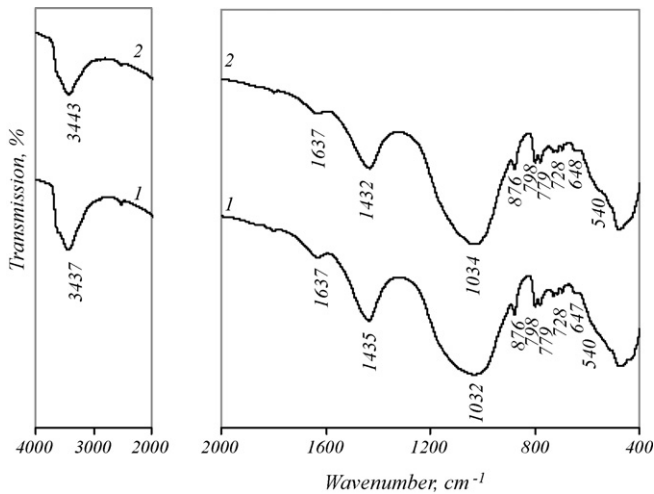
Fig. 3. IR spectra of clay body from Girininkai pit, fired at 600 °C for 0.5 h (1) and 4 h (2).

ones of natural hematite.[8] Thus, we can state that Girininkai clay contains hematite, although this phase was not identified by XRD due to its small amount. It was established that 9% of total iron in Girininkai clay is joint into hematite (Fig. 2b, curve 3).

The mineralogical composition of samples fired at 600 °C changed insignificantly. No peaks of kaolinite were identified since it decomposes at 500–550 °C (Fig. 1a, curve 2).[4] The

amount of Fe_2O_3 is small (13% of the total iron) (Fig. 2b, curve 3), thus we can state that its dark pale colour is predetermined by primary clay minerals and formed feldspars (orthoclase $K(Al,Fe)Si_2O_8$ (d – 0.423, 0.378, 0.324, 0.300 nm)), containing iron (Fig. 1a, curve 2). New bands at 728, 647 cm^{-1} and shoulder at ∼540 cm^{-1} in IR spectra testify about the formation of orthoclase (Fig. 3, curves 1 and 2).[32–34]

The amount of structural Fe^{3+}, if comparing with the one in natural clay, increases up to 76.49%. Its amount increased due to Fe^{2+} oxidation during clay minerals dehydration because only 6% of the Fe^{2+} remained (Fig. 2a, curves 1 and 2).

With increase of duration of isothermal exposure from 0.5 to 4 h at 600 °C temperature, the brightness, the values of red and yellow colour coordinates $b*$, $a*$ of the ceramic body from the Girininkai clay stay almost constant (Fig. 4a, b and c, curve 1), so the colour of the ceramic body (dark pale) is steady too.

X-rays diffraction patterns of clay samples fired at 800 °C show that prolonging the firing duration from 0.5 to 4 h, the intensivity of both, illite and muscovite peaks, decreases (Fig. 1a, curve 3). The ceramic body fired at this temperature blushes because the amount of iron incorporated into hematite Fe_2O_3 increases from 13% (600 °C, 4 h) to 18% (800 °C, 2 h) (Fig. 2b, curve 3 and Fig. 4a, curve 1). However, 68–73% of the iron is in the composition of other compounds, including calcium pyroxene–augite $Ca(Fe,Mg)Si_2O_6$ (d – 0.299, 0.291, 0.252, 0.252 nm), which was formed after complete decomposition of carbonates after 4 h of firing at this temperature (Fig. 1a, curve
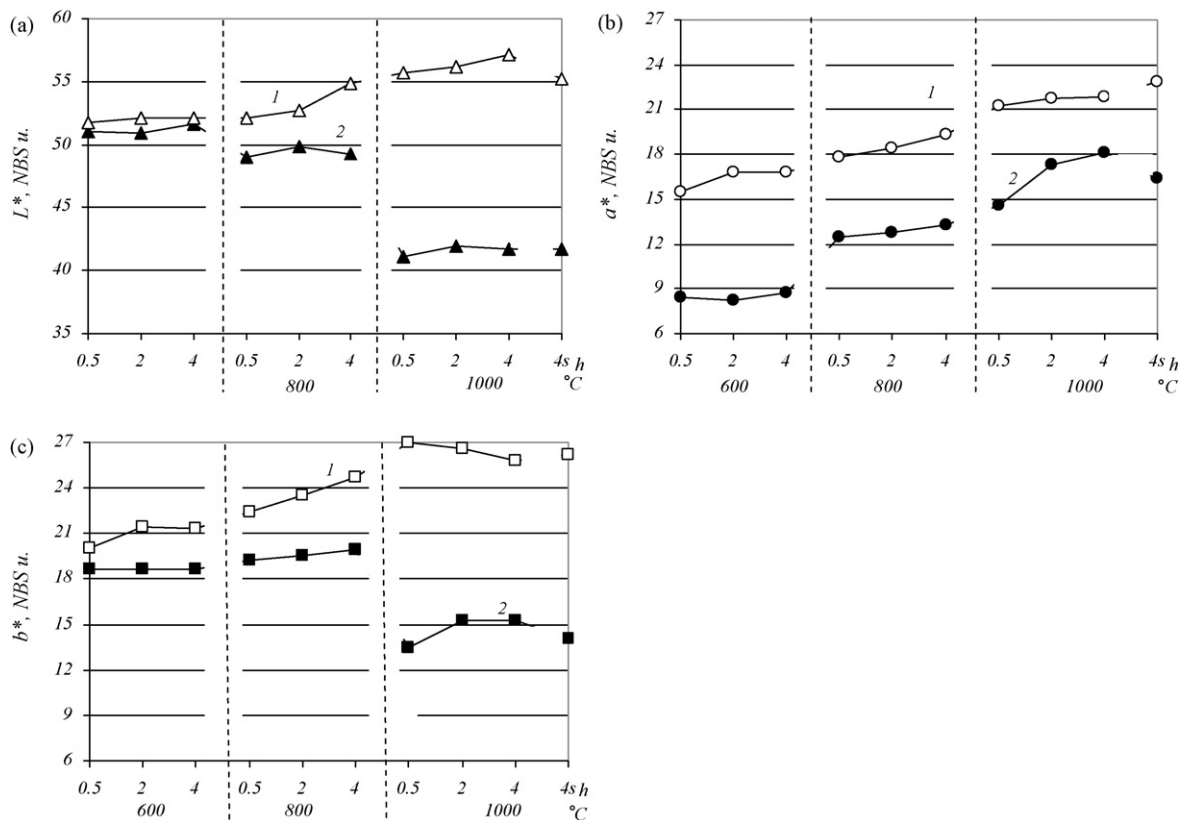

Fig. 4. The influence of firing temperature and duration of isothermal exposure on the lightness $L*$ (a), and on the coordinates of red colour $a*$ (b) and yellow colour $b*$ (c) of a ceramic body. (1) The Girininkai clay, (2) the glauconite rock of the Sventoji, and (4s) samples fired at 1000 °C for 4 h with a constant heating rate 200 °C/h.
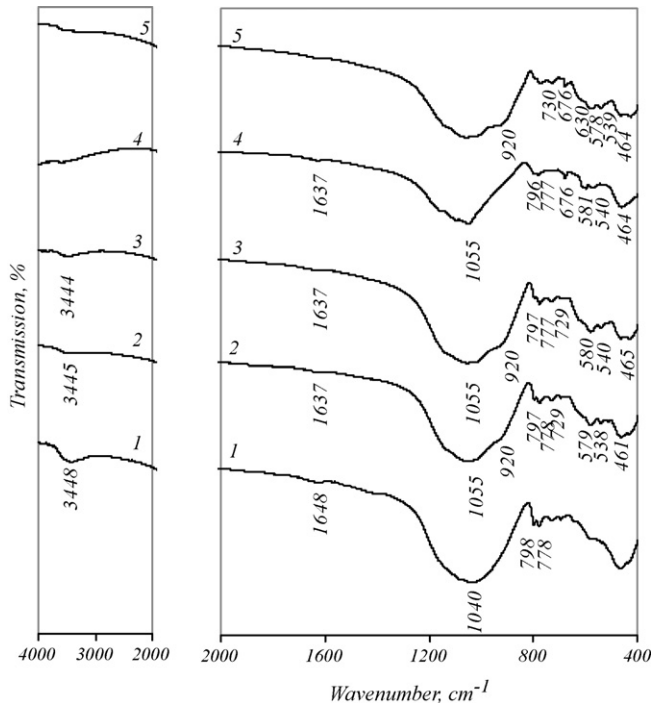
Fig. 5. IR spectra of clay body from Girininkai pit, fired at 800 °C for 4 h (1), at 1000 °C for 0.5 h (2), 2 h (3), and 4 h (4), at 1025 °C for 4 h (5).

3 and Fig. 2a, curve 1). Therefore, the yellow colour prevails (Fig. 4b and c, curve 1). After 2 h of firing at this temperature and after the formation of better crystallized compounds, the ceramic body begins to brighten and in 4 h its brightness value reaches 55 NBS units (Fig. 4a, curve 1). According to Mössbauer analysis data, 9% of the total iron in the ceramic body fired at 600–800 °C is in the form of magnetite (Fig. 2b, curve 4).

The changes of the mineral composition of Girininkai clay during the firing samples at 800 °C can be clearly seen in their IR spectra (Fig. 5, curve 1). After firing the samples for 4 h at 800 °C it was noticed that in the range of hydroxy group symmetric vibrations the band at 3448 cm^{-1} became significantly smaller, and there was only a trace of the band, belonging to δ (H$_2$O) vibrations at the frequency range around 1648 cm^{-1}. At 1040 cm^{-1} absorption band in the range of asymmetric silicate tetrahedron vibrations is broaden and less intensive. This fact shows that hydromica crystal lattice starts its decomposition at 800 °C. After 4 h of firing at 800 °C carbonates are completely decomposed, because there are already no 1435 and 876 cm^{-1} frequency bands in IR spectra (Fig. 5, curve 1 and Fig. 3, curves 1 and 2).[32–34]

Formation reactions of a ceramic body occur rapidly at 1000 °C, at which the following new and more stable compounds (from the point of view of thermodynamics) are crystallized: anorthite, diopside, and cristobalite (Fig. 1a, curve 4). After the decomposition of hydromica, iron is mostly distributed in Fe$_2$O$_3$ (18–20%) and in spinel Mg(Al,Fe)$_2$O$_4$ (28–41%). As a result, the value of red colour coordinate of a ceramic body increases to 21.8 NBS unit (Fig. 2b, curves 3, 5 and Fig. 4b, curve 1). After 4 h of firing at this temperature, after the formation of diopside

(green) in the ceramic body, its yellowish tint given by augite has diminished (Fig. 1a, curve 4 and Fig. 4c, curve 1).

The colour of the ceramic body from Girininkai clay fired at 1025 °C for 4 h is more red, rich and darker (a^* = 23.65 NBS unit, b^* = 24.39 NBS unit, L = 49.64 NBS unit) than the colour of the ceramic body fired at 1000 °C for 4 h (a^* = 21.88 NBS unit, b^* = 25.80 NBS unit, L = 57.07 NBS unit) (Fig. 4a and b, curve 1). The amount of iron in hematite in the ceramic body fired at 1025 °C (50%) is around 5 times bigger, and the amount of Fe^{3+} in structure of compounds (18–19%) around 3–4 times smaller, with respect to the amounts present in natural clay (10 and 65% respectively) (Fig. 2a, curve 1 and Fig. 2b, curve 3).

IR spectra of Girininkai clay fired at 1000 and 1025 °C temperatures support the results of XRD analyses. On the one hand, with prolonging the firing duration and temperature of the samples a decrease of intensity of 798 and 778 cm^{-1} (silica absorption bands doublet) is noticed (Fig. 5, curves 2–5). On the other hand, the absorption bands at 730, 578 and 539 cm^{-1} (which are typical for inside deformations of [SiO$_4$] tetrahedrons) and the shoulder at 920 cm^{-1} (in the range of symmetric and asymmetric stretching of Si–O) testify the formation of anorthite (Fig. 5, curve 2–5).[32,33] Thus we can state that at high temperatures quartz is active in the sintering process of the ceramic body of Girininkai clay and at the same time in the formation of anorthite as stable compound. Formation of diopside in the ceramic body fired at 1000 and 1025 °C temperatures for 4 h is proved by the absorption band at 676 cm^{-1} and by the shoulder at ∼630 cm^{-1}, as the bands defining symmetric and asymmetric vibrations of Si–O in the range of frequencies 800–1200 cm^{-1} are typical for many silicate compounds and it is complicated to identify diopside in this part of IR spectra (Fig. 5, curves 4 and 5).[33] The absorption bands at around 535 and 475 cm^{-1} are typical for hematite.[29,32] However these absorption bands in all IR spectra of clay samples fired at 1000–1025 °C temperatures were overlapped with more intense bands of anorthite or other feldspar (Fig. 5, curves 2–5).

With the increase of firing temperature, the amount of iron in the structure of minerals diminishes, and a greater amount of iron is transformed into hematite and dark brown spinel (Fig. 1a and b, curves 4 and 5; Fig. 2, curves 1, 3 and 5). Due to the above reasons, the colour of the ceramic body changes from pale brown to brown red.

Thus, while increasing the firing temperature of the Girininkai clay from 600 to 1025 °C and duration of isothermal exposure in the firing temperature from 0.5 to 4 h, more iron is incorporated into oxides and the amount of it diminishes in the structure of other compounds, which causes the colour change of the ceramic body. However, in the ceramic body fired at 1000–1025 °C the value of yellow colour coordinate is larger than that of red colour coordinate. The colour of these ceramic bodies belongs to the group of orange colours (according to reflection spectrum wave length) and it is pale.

3.2. Glauconite rock

According to Mössbauer spectrum analysis, almost all iron in Sventoji glauconite rock is in the structure of compounds. The
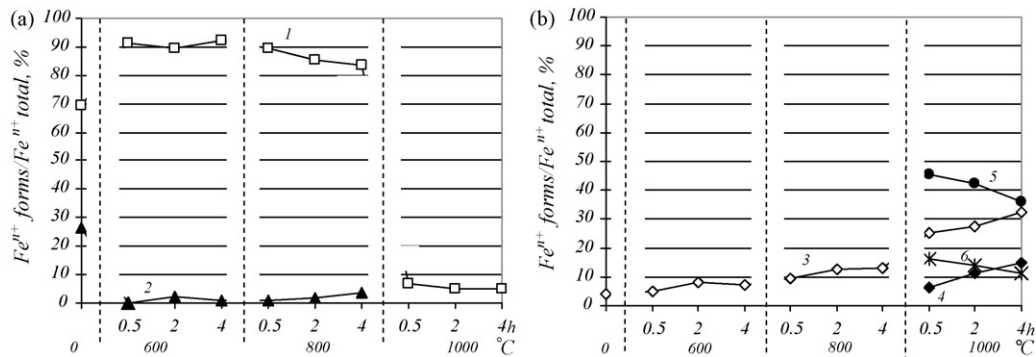
Fig. 6. Dependence of the amount of iron incorporated into the structure of the crystal lattice of compounds (a): Fe^{3+} (1), Fe^{2+} (2) and in oxides (b): Fe_2O_3 (3), Fe_3O_4 (4), $MgFe_2O_4$ (5) and $Fe_{2-x}(Al,Si)_xO_3$ (6) in the ceramic body from Sventoji glauconite rock on the firing temperature and duration of isothermal exposure in it.

amounts of Fe^{2+} and Fe^{3+}, in respect to the total iron present in a sample, are %: 26.58 and 69.45. The amount of iron in hematite is only 3–4% from total amount of iron in glauconite rock (Fig. 6; curves 1–3). The greenish colour of the rock is predetermined by primary minerals (in particular glauconite).

The amount of Fe^{3+} in the glauconite rock of the Sventoji at 600 °C increases to 91%, at 800 °C it diminishes only slightly, whereas at 1000 °C it comprises only 5% of the total iron present in glauconite rock (Fig. 6a, curve 1). The amount of iron in hematite in the samples of the Sventoji glauconite rock fired at 600 °C, increase twice, whereas at 800 °C – three times, comparing it with the one present in raw material (Fig. 6b, curve 3). These changes reflect changes in values of colour coordinates: a^* increased from 8.38 (600 °C 0.5 h) to 13.23 NBS unit (800 °C 4 h), b^* – from 18.66 to 19.93 NBS unit (Fig. 4b and c, curve 2). The green grey colour of glauconite rock takes a yellowish brown tint.

It is measured that glauconite rock became notably darker after firing it at 1000 °C (Fig. 4a, curve 2). In the samples of Sventoji glauconitic rock fired at this temperature, amount of iron in hematite comprises 33% of the iron present in the sample (Fig. 6b, curve 3). When prolonging the firing time from 0.5 to 4 h (at 1000 °C), the colour of glauconite becomes redder, and it can be seen by the value of colour coordinate a^* increasing from 14.60 to 18.08 NBS units and it is bigger than the yellow one. After 0.5 h of firing at 1000 °C, the values of colour brightness L^* become the smallest (Fig. 4a–c, curve 2). At 1000 °C, with increasing the firing exposure, the hematite and magnetite content in glauconite sample consistently increase, the amount of Fe^{3+} in the structure of other compounds varies very slightly, while the content of iron in magnesioferrite $MgFe_2O_4$ decreases (from 45.30 to 36.17%) (Fig. 6b, curve 5). Accordingly, it can be proposed that the samples become redder due to the increase of iron in the form of hematite and magnetite and to the decrease in the form of magnesioferrite. For the first time magnesioferrite was observed in the samples when glauconite rock was fired at 1000 °C for 0.5 h.

After firing glauconitic rock at 1000 °C in its composition (depending on firing time) about 1.5 times more iron is in hematite, 0.8–1.6 times more in magnesioferrite than in $Mg(Al,Fe)_2O_4$ spinel, 2–3 times in magnetite and 3–4 times

less in the structure of other compounds than in the ceramic body of Girinkai clay (Fig. 6 vs. Fig. 2). Therefore, glauconite rock is much darker and redder than the Girininkai clay ceramic body. The values of the yellow colour coordinate b^* of glauconite rock fired at 1000 °C are smaller than the values of the red colour coordinate (Fig. 4 a–c, curves 1, 2).

By summarizing the obtained results, it may be stated that the colour of glauconite rock, while firing it at 600, 800 and 1000 °C, changes from natural green grey into green brown at 600–800 °C and into dark brown at 1000 °C. Therefore, glauconite rock fired at 1000 °C is much darker and redder than the Girininkai clay ceramic body. The tint of glaukonite ceramic body is mainly determined by the amounts of magnetite, hematite and magnesioferrite at a relatively small amount of Fe^{3+} in the structure of other compounds formed during the firing of a ceramic body. Thus, choosing the adequate firing regime the glauconite rock can be used as coloration additive in ceramics production.

3.3. Clay with glauconite additions

The colouring effect of Sventoji glauconite rock depends on the quantity of additive, specific surface area of glauconite rock and firing regime. It is determined that the colour of a ceramic body notably darkens when there is no less than 30% of glauconite rock.[30]

According to Mössbauer spectrum analysis, in the ceramic body of Girinkai clay with 30% of natural glauconite rock additive fired for 4 h at 1000 °C, the amount of iron in magnesioferrite comprises 51.66% of the total iron present in the sample and it is higher than in the spinel that was formed in the ceramic body of Girininkai clay fired at the same regime (41.08%) (Table 2 and Fig. 2a, curve 5). Furthermore the amount of Fe^{3+} in the structure of compounds decreases from 29.29 to 20.76% of the total iron, but this change is probably too low to reduce the yellowish tint of the ceramic body, usually tinged by these compounds (as augite) (Tables 2 and 3). As a result, the ceramic body darkens, but the value of a yellow colour coordinate is unchanged. The decrease of iron in the structure of compounds could influence and change the red colour. The red colour is fading though the amount of iron in the hematite is by 4% points smaller than in Girininkai clay (Table 3).

Table 2
Dependence of the amount of iron incorporated into the structure of the crystal lattice of compounds: Fe^{3+}, Fe^{2+} and in oxides: Fe_2O_3, Fe_3O_4, $MgFe_2O_4$, $Fe_{2-x}(Al,Si)_xO_3$ on the composition of moulding mixtures and firing regime.

Additive		Burning regime			Amount (%)					
Amount (%)	Specific surface area (m^2/kg)	Temperature (°C)	Duration (h)	The rise in temperature (°C/h)	Fe^{2+}	Fe^{3+}	Fe_2O_3	Fe_3O_4	$MgFe_2O_4$	$Fe_{2-x}(Al,Si)_xO_3$
30	50	1000	4	500	–	20.76	21.43	1.32	51.66	4.83
50	50	1000	4	500	–	14.63	27.07	5.17	46.42	6.71
30	250	1000	4	500	–	19.54	23.19	4.09	48.91	4.27
30	250	1000	4	200	–	16.20	24.58	1.54	52.98	4.79
30	250	1025	4	500	–	17.97	24.43	6.43	48.24	4.26
50	250	1000	4	500	–	14.67	28.11	6.72	45.15	5.35
50	250	1000	4	200	–	13.49	28.96	2.65	50.69	4.21
50	250	1025	4	500	–	12.41	28.32	4.72	49.42	5.13
30	350	1000	4	500	–	19.39	28.70	14.46	32.80	4.65
30	350	1025	4	500	–	16.19	31.16	15.89	31.93	4.83
50	350	1000	4	500	–	14.70	25.17	16.26	37.90	5.97

Table 3
Dependence of the coordinates of the red and yellow colours $a*$, $b*$ and of the colour lightness $L*$ of the ceramic body with Sventoji glauconite rock additive fired at 1000 °C for 4 h on the amount of additive, its specific surface area and the heating rate.

Amount (%)	Specific surface (m^2/kg)	The rise in temperature (°C/h)	Coordinates of colour (NBS u.)		
			$L*$	$a*$	$b*$
0		500	57.07	21.88	25.80
30	50	500	54.21	23.42	25.96
50	50	500	51.46	23.09	24.66
30	50	500	54.21	23.42	25.96
30	50	200	53.63	23.01	25.35
30	250	500	53.22	22.31	24.88
30	250	200	54.07	22.61	25.79
30	350	500	51.48	23.66	23.80
30	350	200	52.45	23.49	26.14

With the increase of specific surface area of glauconite rock additive and the increase of firing temperature of the samples from 1000 to 1025 °C a general tendency has been noticed: the amount of iron in the composition of magnesioferrite decreases, but it increases in hematite and especially in magnetite (up to 16.26%). There is less Fe^{3+} present in the structure of other compounds (Table 2). These results are confirmed by XRD analyses data. In X-ray diffraction patterns of the mixtures with coarse glauconite additive ($S_a = 250$ m^2/kg) the peaks of magnetite cannot be identified due to a small amount of this compound. Moreover, the main peaks of hematite (d – 0.270, 0.251, 0.169, 0.148 nm) are less intensive (Fig. 7, curves 1 and 3) than in the patterns of the mixtures with finer ($S_a = 350$ m^2/kg) additive. In this case it is already possible to distinguish the small peaks of magnetite (d – 0.296, 0.252, 0.209, 0.161 nm) (Fig. 7, curves 2 and 4). The interplanar distances of magnesioferrite (d – 0.296, 0.253, 0.209, 0.161 nm) and also augite are close to interplanar distances of other compounds, so the XRD data can only note the fact of their formation, but not the peak intensity changes. An analogous tendency, but to a lesser degree, can be evidenced by increasing the firing temperature of the samples (Fig. 7, curves 3 and 4).

By increasing the specific surface area of glauconite rock from 50 to 350 m^2/kg, the values of yellow colour coordinates diminish and differ from one another by approximately 0.8–1

percentage points, the colour of ceramic body darkens by 1–1.7 percentage points and takes the colour typical of the mixture of these compounds (Table 3).

A similar effect has the rate of temperature raising on the colour of the clay body containing glauconite rock additive. As may be observed (Table 3), the colour of the samples fired with a 500 °C/h rate is darker (for specific surface values above 50 m^2/kg) than that of samples fired with a 200 °C/h rate. Moreover, with a slower heating rate of the ceramic body, the amount of hematite changes insignificantly, thus, the value of red colour coordinate remains almost unchanged. However, after reducing the amounts of structural Fe^{3+} and magnetite, the ceramic body becomes "brighter", and the colour poorer (Tables 2 and 3).

Thus, it may be stated that the ceramic body from Girininkai clay with the additive of Sventoji glauconite rock (independently on its thinness and firing regime) contains 1.4–2.6 times less Fe^{3+} in the structure of other compounds than the ceramic body from natural clay. When natural and roughly ground glauconite rock ($S = 50$ and 250 m^2/kg) is used, the amount of iron in hematite and magnetite varies a little. Only after grinding the glauconite rock into smaller particles ($S = 350$ m^2/kg), the amount of iron in hematite increases by 1.1–1.2 times and in magnetite by 3–3.5 times. With the increase of the specific surface of the glauconite rock additive and the firing temperature of the samples, the amount of iron present in the composition of magnesioferrite
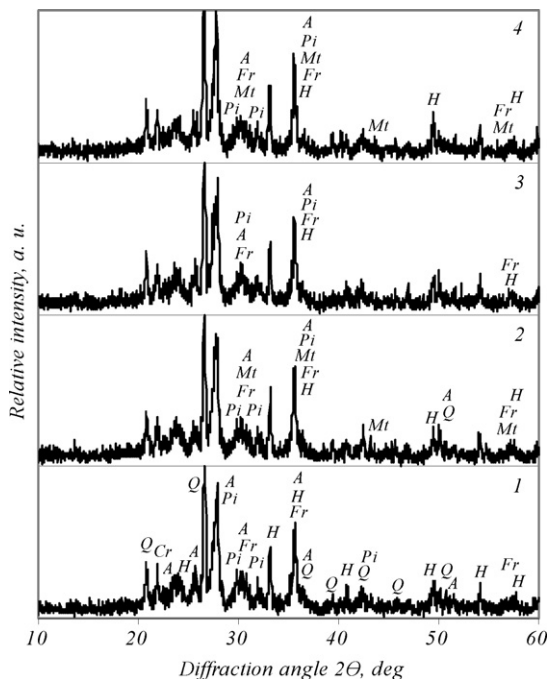
Fig. 7. X-ray diffraction paterns of ceramic body with 30% glauconite rock additive, fired at 1000 °C (1 and 2) and 1025 °C (3 and 4) for 4 h. $S_a = 250 \, m^2/kg$ (1 and 3) and $S_a = 350 \, m^2/kg$ (2 and 4). *Indexes*: Q, quartz; A, anorthite; H, hematite; Fr, magnesioferrite; Cr, cristobalite; Pi, augite; Mt, magnetite.

gradually decreases (1.6 times). All the changes in the mineral composition that influence and determine the nicely red colour can be noticed only after grinding the additive of Sventoji glauconite to $350 \, m^2/kg$ of the specific surface and adding no less than 30% of it into the forming mass.

4. Conclusions

1. While increasing the firing temperature of the Girininkai clay from 600 to 1025 °C and duration of isothermal exposure in the firing temperature from 0.5 to 4 h, the amount of iron in hematite increases 5 times, whereas the amount of Fe^{3+} incorporated into the crystal lattice of other compounds diminishes 3–4 times if compared with natural clay.
2. The red colour of a ceramic body is mainly determined by the amount of hematite. When the amount of iron in this compound increases from 18% (at 800 °C, for 2 h) to 49% (at 1025 °C, for 4 h), the value of red colour coordinate increases from 18.44 to 23.65 NBS units. If during firing spinel is formed together with hematite, the ceramic body darkens and becomes redish brown.
3. Glauconite rock fired at 1000 °C is much darker and redder than Girininkai clay fired at the same temperature, since there is 1.5 times more iron in hematite, 1–1.6 times more in spinels, 2–3 times more in magnetite and 2–6 times less in the structure of other compounds.
4. The colour of the ceramic body notably darkens when there is no less than 30% of glauconite rock with a specific surface area of $350 \, m^2/kg$, since the amount of iron in hematite and magnetite is bigger than in natural clay body. With decreasing

of Fe^{3+} amount in the structure of compounds the ceramics shows up a typical colour of the mixture of hematite, magnetite and magnesioferrite minerals.

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