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Peculiarities of Glass Ceramics Formation from Red Clay– Cullet–Waste Activated Sludge–Hematite Mixtures

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Abstract:

In the work, an analysis of the phase formation process proceeding in a quaternary red clay–low-melting cullet–iron oxide (Fe_2O_3)–WAS (waste activated sludge) system in treatment at 1000°C in air has been performed. It has been established that, in sintering of the mixtures, porous ceramics consisting of a glass phase alloyed with iron ions with inclusions of cristobalite, iron-containing silicates of complex composition, α -Fe₂O₃, and an insignificant amount of Fe₃O₄ forms. The porous glass ceramics meets the compressive strength requirements imposed on building bricks.

Keywords: *Red clay; Cullet; Fe*₂*O*₃*; Sintering; Glass ceramics.*

1. Introduction

Products manufactured from red clay, in particular bricks, are extensively used in the construction industry throughout the world for many centuries. This is why, in many regions of the world, there currently exists shortage of natural raw materials (plastic clay) of necessary quality for the manufacture of conventional building bricks. In this connection, ceramic production engineers faced the problem of replacement a part of clay by anthropogenic wastes. Note that this problem is connected with the problem of reclamation of wastes contaminating the environment. In the first step, the introduction of solid wastes into clay was considered [1-10], and, subsequently, as additives, particularly, pore-forming agents, biowastes were introduced [11-13]. It should be noted that the brick production is power-intensive [14,15]. This is why to decrease the sintering temperature and sintering time, it was proposed to introduce low-fusing agents in the form of feldspars, low-melting glass wastes [12,13], iron-rich glasses, or iron oxide additives into initial clay [16-22].

In [13], it was established that, on the basis of red clay–low-melting cullet–waste activated sludge (WAS) mixtures, it is possible to obtain bricks products of different porosity with good strength properties. In view of the important role of iron additives in the formation of operational properties of brick products, the aim of the present work is to investigate the influence of iron oxide (Fe₂O₃) additives on the phase formation process in sintering of the indicated mixtures in air, to determine properties, and establish the fields of application of the synthesized material.

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2. M	laterials	and H	xperime	ental F	Procedures
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N	Composition as two double	Composition in the form of a general mixture						
specimen	mixtures							
Ι	(80% clay + 20% glass) +	40% clay + 10% glass + 20% WAS + 30% Fe ₂ O ₃						
	$(40\% \text{ WAS} + 60\% \text{ Fe}_2\text{O}_3)$							
II	(80% clay + 20% glass) +	40% clay + 10% glass + 25% WAS + 25% Fe ₂ O ₃						
	$(50\% \text{ WAS} + 50\% \text{ Fe}_2\text{O}_3)$							
	(80% clay + 40% glass) +	40% clay + 10% glass + 30% WAS + 20% Fe ₂ O ₃						
III	$(20\% \text{ WAS} + 40\% \text{ Fe}_2\text{O}_3)$							
IV	(60% clay + 40% glass) +	30% clay + 20% glass + 20% WAS + 30% Fe ₂ O ₃						
	$(40\% \text{ WAS} + 60\% \text{ Fe}_2\text{O}_3)$							
V	(60% clay + 40% glass) +	30% clay + 20% glass + 25% WAS + 25% Fe ₂ O ₃						
	$(50\% \text{ WAS} + 50\% \text{ Fe}_2\text{O}_3)$							
VI	(60% clay + 40% glass) +	30% clay + 20% glass + 30% WAS + 20% Fe ₂ O ₃						
	$(60\% \text{ WAS} + 40\% \text{ Fe}_2\text{O}_3)$							
VII	(50% clay + 50% glass) +	25% clay + 25% glass + 20% WAS + 30% Fe ₂ O ₂						
, 11	$(40\% \text{ WAS} + 60\% \text{ Fe}_2\text{O}_2)$							
VIII	(50% clay + 50% glass) +	25% clay + 25% glass + 25% WAS + 25% Fe ₂ O ₃						
	$(50\% \text{ WAS} + 50\% \text{ Fe}_2\text{O}_3)$,						
IX	(50% clay + 50% glass) +	25% clay + 25% glass + 30% WAS + 20% Fe ₂ O ₃						
	$(60\% \text{ WAS} + 40\% \text{ Fe}_2\text{O}_3)$							

Tab. I Composition of mixtures used for preparation of blanks (wt%).

In the present work, bricks obtained from powdered red clay-milled glass (cullet)– WAS-Fe₂O₃ mixtures were studied. In Table I, the compositions of mixtures are given in the following forms: (a) as a mixture of two compositions (red clay + milled glass) + (WAS + Fe₂O₃); (b) as an generalized mixture. The particle size of glass was 60 μ m $\leq d \leq 250 \mu$ m. Waste activated sludge (biowaste) containing water was used as a plasticizer for powder mixtures. In Table II, the chemical composition of the used materials is presented. Plastically molded laboratory briquettes with sizes $120 \times 60 \times 20$ mm were burnt at a temperature of 1000° C for 10 h in air.

Component		Content, wt%									
	SiO ₂	Fe ₂ O ₃	Al ₂ O ₃	K ₂ O	CaO	Na ₂ O	TiO ₂	P_2O_5	MgO	MnO	Σ
Clay	97.30	1.13	0.81	0.34	0.16	-	0.13	0.05	0.04	0.01	0.13
Glass	72.81	1.08	0.29	0.45	11.29	13.25	0.14	0.03	0.5	0.02	0.15
WAS	organic	organic material: 80.20; clay + sand: 19.80									

Tab. II Chemical composition of used components.

For a better understanding of phase transformations proceeding in quadruple mixtures, individual components and binary mixtures were heat treated at $T_{\rm tr}$ of 800, 900, and 1000°C for 1 and 10 h.

The synthesized products were investigated by X-ray diffraction (XRD) in Cu K α radiation (a DRON-3M diffractometer). SEM and EDS measurements were carried out with a LEO 1450VP scanning electron microscope. Water absorption was determined by the following formula: W, $\% = 100 - [(P_1 - P_0)/P_0] \cdot 100$, where P_0 is the initial weight of a specimen and P_1 is the weight of the specimen after water absorption. The linear electric resistance was measured by the two-point method using a digital multimeter with a capacitance up to 200 M Ω . The electric resistivity (ρ) of specimens was calculated by the formula:

$$\rho \left(\Omega \cdot \mathbf{m} \right) = \frac{RS}{L},$$

where $R(\Omega)$ is the linear electric resistance; $S(m^2)$ is the cross-sectional area of specimens, and L(m) is the length of the specimens. Compression and fracture tests were performed by standard techniques [23].

3. Results and Discussion3.1 Characterization of initial materials



Fig. 1. Fragments of diffraction patterns of used clay, Fe₂O₃, glass, and WAS in the initial state (a) and after treatment at 1000°C for 1 h (b). m is montmorillonite, c is cristobalite, f is feldspar, s is sillimanite, q is quartz, and s_p is Al–Si–O spinel.

According to the XRD data (see Fig. 1a), the used clay contains montmorillonite, cristobalite, and feldspar. Glass is represented by an amorphous phase in the form of diffusion

halo. WAS is characterized by an amorphous phase with a small content of minerals, namely, clay and sand. Iron oxide corresponds to α -Fe₂O₃. After treatment at $T_{tr} = 1000^{\circ}$ C for $t_{tr} = 1$ h (see Fig. 1b), red clay transforms into aluminosilicate ceramics (sillimanite) with impurities such as cristobalite and feldspar. The amorphous state of glass does not change. As a result of the pyrolysis of WAS and the burnt-out of the organic part in the form of CO/CO₂↑, in the solid residue, components corresponding to red clay with sand additives (sillimanite, quartz, and feldspar) are recorded.

3.2 Characterization of specimens from binary mixtures

3.2.1. X-ray data



After $T_{tr} = 1000^{\circ}C$, $t_{tr} = 1 h$

Fig. 2. Fragments of diffraction patterns of specimens obtained from clay–glass (a), clay–WAS (b), and clay–Fe₂O₃ (c) mixtures after treatment at 1000°C for 1 h (b). s is sillimanite, q is quartz, c is cristobalite, f is feldspar, s_p is Al–Si–O spinel, o is Fe₂O₃.

The X-ray diffraction data of specimens obtained by temperature treatment of binary mixtures are shown in Fig. 2. In the heat-treated clay–Fe₂O₃ mixture (Fig. 2a), sillimanite, cristobalite, quartz, and iron oxide (α -Fe₂O₃) are recorded. The heat treatment of the clay–WAS mixture (Fig. 2b) is accompanied by the formation of main phases such as quartz, sillimanite, and cristobalite. After heat treatment of the clay–glass mixture, feldspar, Al–Si–O spinel, and the glass phase are present along with sillimanite and quartz (Fig. 2c). In heating of the WAS–Fe₂O₃ mixture, a composition similar to that formed in treatment of the clay–Fe₂O₃ mixture (Fig. 2d), but in this material, iron oxide dominates. It can be concluded that, during heat treatment of binary mixtures, main phase transformations occur due to the dehydration of clay. The exception is the clay–glass mixture. The appearance of a substantial amount of feldspar and spinel indicates that, in heating up to 1000°C, processes of interaction between the liquid glass phase and products of decomposition of the clay mineral occur, and, in cooling, spinel and feldspar crystallize.

A more detailed investigation of the WAS–Fe₂O₃ binary mixture shows (Fig. 3) that its temperature treatment in the range 800-1000°C is accompanied by a change in the intensity of peaks of α -Fe₂O₃ and the appearance of weak peaks of Fe₃O₄ and halo in specimens (Figs. 3a,a',c,c'). These changes depend on the WAS content in the initial mixtures and, ultimately, on the content of the formed products of thermodestruction of WAS, namely, carbon and CO/CO₂. The formation of Fe₃O₄, which promotes the formation of the glass phase, may be the cause of formation of the amorphous phase (halo) in the specimens treated at 800 and 1000°C [12–18]. Favorable reducing conditions of the transition Fe₂O₃ \rightarrow Fe₃O₄ can be the most probable cause of the absence of a halo in the specimens treated 900°C. In Figs. 3b, b', it is seen that, precisely at this temperature, an increase in the Fe₃O₄ content (see the intensity of the peak at 2 Θ =57.63°) is noted.



Fig. 3. Fragments of diffraction patterns (a–c) and intensity of peaks (a'–c') for specimens obtained from WAS–Fe₂O₃ mixtures at $T_{tr} = 800^{\circ}$ C (a), $T_{tr} = 900^{\circ}$ C (b), and $T_{tr} = 1000^{\circ}$ C (c). $t_{tr} = 1$ h. In a'–c': (1) for α -Fe₂O₃ ($2\Theta = 33.16^{\circ}$); (2) for Fe₃O₄ ($2\Theta = 57.63^{\circ}$); (3) halo.

3.2.2. SEM/EDS data.

The results of the EDS analysis indicate that, in heat treatment of the x% WAS+ y% Fe₂O₃ mixtures, powders and cakes containing Si, Al, Fe, O, and C (Fig. 4) form. In WAS, elements such as Si, Al, and C were present. From the comparison of the content of elements in the specimens (see data of tables shown in Fig. 4) it follows that the most favorable conditions of reduction of Fe₂O₃ are realized in treatment at 1000°C. With increase in the WAS content in the specimens, a large iron content and a small oxygen content are registered. From a comparison of the tabulated data presented in the right part of Fig. 4, it can be concluded that as the WAS content increases, the reduction process Fe₂O₃ \rightarrow Fe₃O₄ \rightarrow Fe is gradually intensified. This is caused by the increase in the content of C and CO in heat treatment. Judging from the microanalysis data, the formation of amorphous iron turns out to be the most probable cause of the appearance of the halo in the X-ray diffraction patterns (see Fig. 3c,c').



T_{tr} = 1000°C, 1 h, air

Fig. 4. Distribution of elements in specimens obtained from x% WAS + y% Fe₂O₃ binary mixture (a) and contents of elements (b) according to EDS data of in the map regime.

3.3 Characterization of specimens from quadruple mixtures

3.3.1. X-ray data



Fig. 5. Fragments of diffraction patterns of specimens obtained from quadruple mixtures at $T_{sint} = 1000^{\circ}$ C, $t_{sint} = 10$ h.

According to the XRD data, in the specimens sintered at 1000°C, intensive halo of an amorphous phase and a number of narrow peaks assigned to hematite (α -Fe₂O₃), cristobalite (SiO₂), and silicates of complex composition are recorded [24,25] (see Fig. 5). Depending on the initial composition of the quadruple mixture and the ratio of the components, the intensities of the halo and narrow peaks (of the crystalline phases) change (Fig. 6). The interrelation between the change in the intensity of the halo and the change in the intensity of the peak of cristobalite, even its disappearance, and the formation of silicates of different type containing Ca, Mg, Al, and Fe indicate the development of the processes of interaction between the components in the sintering process. This is possible in the case of liquid-phase sintering, formation of eutectics, and subsequent precipitation of crystalline phases from eutectic melt in cooling [26,27]. Since the initial mixtures contain low-melting glass with $T_{melting} \sim 800^{\circ}$ C, the processes of interaction of more refractory components must proceed precisely with the glass melt. As a result, glass of another composition must form, and new crystalline phases must precipitate in cooling. The change in the shape of the halo (of the glass phase) agrees with this assumption.



Fig. 6. Change in the intensity of diffraction peaks and halo of specimens obtained from quadruple mixtures at $T_{sint} = 1000^{\circ}$ C, $t_{sint} = 10$ h. (1) cristobalite ($2\Theta = 21.48^{\circ}$); (2) complex silicate 1 ($2\Theta = 27.80^{\circ}$); (3) complex silicate 2 ($2\Theta = 30.10^{\circ}$); (4) hematite ($2\Theta = 33.16^{\circ}$); (5) halo.

3.3.2. SEM/EDS data

The data of SEM investigations show that specimens have an irregular porous structure (see Figs. 7-9, scale 100 µm). The pore size has a wide range of variation from $d \le 0.5$ µm up to $d \le 100$ µm. Nevertheless, it can be concluded that the number of pores, their size, shape, and distribution depend on the content of clay, glass, iron oxide, and WAS in the initial mixtures. For instance, the decomposition of the clay mineral is accompanied by its dehydration, dihydroxylation, and release of water vapor [28–31]. During burnt-out of WAS, CO/CO₂ are evolved. Both these processes promote pore formation. At the same time, the formation of low-viscosity melt leads to the partial filling of interconnecting and open pores, thus reducing the porosity of the specimens. Precisely the combination of these processes (pore formation and filling of pores by melt) and the domination of one process over the other predetermine the porous structure of the material. The analysis of the micrographs shown in Figs. 7-9 (scale 10 µm) and XRD data enable us to establish that the sintered materials is a glass phase. At specimen's destruction, large fragments and agglomerates of smaller particles

are formed. This is most clearly seen in Fig. 9, IX. According to the EDS analysis data (see Figs. 7a-9a, scale 10 μ m, histograms on side **b**, and Tables III-V), these agglomerates contain much iron. But in large fragments (glass phase) the iron content is lower. The glass phase is represented by elements that enter into the compositions of both primary glass and clay. It can be concluded that the fracture of specimens occurs at the places of accumulation of iron oxide particles, which precipitate from melt in its cooling. The EDS analysis in the map regime (Fig. 10) showed the existence of some in homogeneity in the distribution of elements in the material of the specimen. For example, a slightly increased concentration of the elements Fe and O in the region of propagation of cracks was noticed. Small areas of concentration of the elements Si, Ca, Al, and C were also recorded. These data indicate the places of localization of silica, silicates of complex composition, and carbon in the glass phase.



Fig. 7. Micrographs of fractures of (80 wt% clay + 20 wt% glass) + (x wt% WAS + y wt% Fe_2O_3) specimens (side a in Fig. 7) and results of local EDS analysis (side b in Fig. 7).



Fig. 8. Micrographs of fractures of (60 wt% clay + 40 wt% glass) + (x wt% WAS + y wt% Fe_2O_3) specimens (side a in Fig. 8) and results of local EDS analysis (side b in Fig. 8).



Fig. 9. Micrographs of fractures of $(50 \text{ wt\% clay} + 50 \text{ wt\% glass}) + (x \text{ wt\% WAS} + y \text{ wt\%} \text{ Fe}_2O_3)$ specimens (side a in Fig. 9) and results of local EDS analysis (side b in Fig. 9).



Fig. 10. Distribution of elements in a specimen obtained from (80 wt% clay + 20 wt% glass) + (50 wt% WAS + 50 wt% Fe₂O₃) mixture. EDS in the map regime.

I. $(80\% \text{ clay} + 20\% \text{ glass}) + (40\% \text{ WAS} + 60\% \text{ Fe}_2\text{O}_3)$		II.(80% clay + (50% WAS + 5	- 20% glass) + 0% Fe ₂ O ₃)	III. (80% clay (20% WAS +	Local place		
	Element	Weight%	Element	Weight%	Element	Weight%	
	O K	36.86	C K	1.93	O K	61.03	
	Al K	3.43	O K	45.11	Al K	0.10	
	Si K	38.79	Na K	3.36	Si K	0.99	
	Ca K	5.22	Al K	2.99	Ca K	30.45	
	Fe K	15.71	Si K	28.26	Fe K	7.42	1
			Ca K	3.39			
			Fe K	14.77			
	Totals	100.00	Totals	100.00	Totals	100.00	
	O K	47.08	O K	31.98	C K	1.31	
	Na K	2.37	Na K	2.79	O K	45.03	
	Al K	2.23	Al K	2.13	Al K	3.70	
	Si K	33.88	Si K	27.28	Si K	7.58	2
	Ca K	3.16	Ca K	2.29	Ca K	18.64	2
	Fe K	11.28	Fe K	33.53	Fe K	23.75	
	Totals	100.00	Totals	100.00	Totals	100.00	
	O K	28.21	C K	3.98			
	Al K	2.85	O K	16.44			
	Si K	33.39	Na K	1.39			
	Ca K	12.59	Al K	0.42			
	Fe K	22.96	Si K	6.10			3
			Ca K	1.00			
			Fe K	70.48			
	Totals	100.00	Totals	100.00			

Tab. III Content of elements in local places of specimens (80 wt% clay + 20 wt% glass) + (x wt% WAS + y wt% Fe_2O_3).

Tab.	IV	Content o	f elements	in local	places	of spec	cimens	(60wt%	clay -	+ 40 v	vt%	glass)	+ (x
wt%	WA	AS + y wt%	6 Fe ₂ O ₃).										

IV.(60% clay + 40% glass) + (40% WAS + 60% Fe ₂ O ₃)		V.(60% clay + (50% WAS + 5	40% glass) + 50% Fe ₂ O ₃)	VI. (60% clay - (60% WAS + 4	Local place	
Element	Weight%	Element	Weight%	Element	Weight%	
C K	4.90	C K	6.44	C K	6.87	
O K	58.42	O K	38.86	O K	37.20	
Na K	0.06	Na K	3.17	Na K	0.81	
Al K	1.20	Al K	2.34	Al K	2.48	
Si K	28.17	Si K	29.45	Si K	43.89	1
Ca K	10.71	Ca K	2.46	Ca K	0.94	
Fe K	1.54	Fe K	17.27	Fe K	3.00	
Totals	100.00	Totals	100.00	Totals	100.00	
O K	31.55	C K	3.41	C K	7.16	
Si K	40.28	O K	36.44	O K	39.57	
Ca K	17.21	Na K	1.85	Na K	0.06	
Fe K	10.95	Al K	1.51	Al K	2.07	2
		Si K	16.08	Si K	3.62	2
		Ca K	3.89	Ca K	36.78	
		Fe K	36.82	Fe K	10.74	
Totals	100.00	Totals	100.00	Totals	100.00	
C K	2.62	C K	3.47			
O K	44.07	O K	40.83			
Na K	0.92	Na K	2.20			
Al K	0.70	Al K	1.80			
Si K	33.33	Si K	24.72			3
Ca K	13.93	Ca K	11.54			
Fe K	4.44	Fe K	15.44			
Totals	100.00	Totals	100.00			

						r
VII. (50% clay + 50% glass) + (40% WAS + 60% Fe ₂ O ₃		VIII. (50% cla + (50% WAS	ay + 50% glass) + 50% Fe ₂ O ₃)	IX. (50% clay + (60% WAS + 4	Local place	
Element	Weight%	Element	Weight%	Element	Weight%	1
O K	47.58	C K	0.04	C K	2.21	
Na K	2.94	O K	8.79	O K	43.23	
Al K	2.12	Na K	0.07	Na K	3.27	
Si K	29.77	Si K	14.08	Al K	0.69	
Ca K	4.75	Ca K	39.32	Si K	37.95	1
Fe K	12.84	Fe K	37.70	Ca K	11.76	
				Fe K	0.39	
Totals	100.00	Totals	100.00	Totals	100.00	
O K	48.31	C K	1.40	C K	3.81	
Na K	2.21	O K	30.74	O K	18.99	
Al K	3.52	Na K	1.35	Na K	0.78	
Si K	25.46	Al K	2.84	Al K	0.56	
Ca K	3.96	Si K	24.19	Si K	23.79	2
Fe K	16.33	Ca K	6.48	Ca K	5.01	
		Fe K	32.99	Fe K	47.07	
Totals	100.00	Totals	100.00	Totals	100.00	
C K	3.62	C K	4.06			
O K	29.89	O K	23.89			
Na K	1.52	Na K	1.28			
Al K	0.70	Al K	3.68			
Si K	17.38	Si K	39.17			3
Ca K	3.93	Ca K	6.80			
Fe K	41.44	Fe K	21.12			
Totals	100.00	Totals	100.00			

Tab. V Content of elements at local places of specimens $(50 \text{ wt\% clay} + 50 \text{ wt\% glass}) + (x \text{ wt\% WAS} + y \text{ wt\% Fe}_2O_3).$

Thus, the sintering of the quadruple compositions is accompanied by the formation of the amorphous material (glass) of complex composition [3] containing carbon, iron, Fe_2O_3 and SiO_2 particles that crystallized from the melt, and silicates containing Ca, Mg, Al, and Fe. In other words, during sintering of quadruple clay–cullet–iron oxide–WAS mixtures, glass ceramics of complex composition forms. The final composition of the glass phase depends of the content of the components in the initial mixtures. The Fe_2O_3 and WAS additives play a particular role in the formation of the glass phase in the stage of preparation of mixtures. Transforming into carbon, WAS promotes the transitions of a part of ferric iron into ferrous iron in the glass melt, thus facilitating the accumulation of the liquid phase. As a result, the strength of the sintered sample must increase.

3.3.3. Absorption properties of specimens

Since the synthesized glass ceramics has a porous structure (see Figs.7-9), which somewhat changes depending on the composition of the initial mixtures, the absorption properties also must change. The performed investigations on water absorption showed that with increase in the glass content in the initial mixtures at a constant content of WAS–Fe₂O₃, water absorption decreased (Fig. 11, I). This is due to the capability to fill pores by the liquid glass phase, namely, by the viscosity and amount of melt, and by the size of pores formed in synthesis. At the same time, water absorption of the specimens decreases at a constant clay–glass content and a decreasing WAS content in the initial mixtures (Fig. 11, II) because the content of the pore-forming agent, i.e., WAS decreases (WAS + $O_2 \rightarrow CO/CO_2\uparrow$).



Fig. 11. Change in the value of water absorption in synthesized specimens depending on the contents of glass (I) and WAS (II) in initial mixtures.

3.3.4. Compressive strength of specimens

The compression tests of specimens showed (Fig. 12) that the value of $R_{\rm comp}$ depended on the composition of the initial mixtures. For most specimens, the ultimate compressive strength either agrees with the standard value taken for building bricks (~100 kg/cm²) or exceeds this value despite the high porosity of specimens (see Table VI, Figs. 6-9, 11). The cause of the increased strength of specimens is the formation of iron-containing glass exhibiting increased strength [29,32].



Fig. 12. Change in the compressive strength of specimens depending on the contents of glass (I) and WAS (II) in initial mixtures.

	With use	of water	With use	e WAS	With use of WAS + Fe_2O_3		
Mixture Type, wt%	F _{comp.} , Kg/cm ²	W, %	F _{comp.} , Kg/cm ²	W, %	F _{comp.} , Kg/cm ²	W, %	
Red clay (standard)	75 – 100	3 – 7					
80 rc – 20 g	79	5	75	12	110 – 190	30 - 7	
60 rc - 40 g	110	4	98	6	115 – 198	20 - 5	
50 rc – 50 g	110	1	103	2	100 - 167	8-6	

Tab. VI Properties of bricks obtained from red clay with use of different additives. $T_{sint.} = 1000^{\circ}C$, $t_{sint} = 10$ h. Sintering on air.

Note: rc is red clay, g is glass

3.3.5. Electrophysical properties of specimens

In the investigation of the electric conductivity of the ceramic specimens, it was established that they had resistive properties (Fig. 13). With decrease in the clay content and increase in the glass content in the initial mixture, ρ of the ceramics specimens decreases from ~550 $\cdot 10^3$ down to ~80 $\cdot 10^3 \Omega$ m (see Fig. 13, I and Table I). It can be expected that this is due to not only the formation of the iron-containing glass phase, but also to the presence of carbon and iron oxide inclusions in the glass phase. As it follows from Fig. 13, II, with decrease in the specimens obtained from the mixtures with a WAS content of 50 wt.%, a deviation from this regularity is noted (see Fig. 12, II, a,b). This is possibly caused by the formation of two different types of glasses, as evidenced by the change in the shape of the halo in the X-ray diffraction patterns (see Fig. 5 b,c) and by the change in the mechanism of electric conduction [33–35].



Fig. 13. Change in the resistive properties of specimens depending on the contents of clay (I) and WAS (II) in initial mixtures.

4. Conclusion

Treatment of mixtures consisting of clay, low-melting cullet, iron oxide (Fe₂O₃), and WAS (waste activated sludge) at 1000° C in air is accompanied by the practically simultaneous course of the following processes:

- the pyrolysis of WAS with the release of vaporous/gaseous products of thermodestruction and formation of low-ordered carbon;
- the dehydration and dehydroxylation of clay with the release of water vapor;
- the formation of a glass phase of new composition alloyed with Fe as a result of the interaction of the glass melt with iron oxide particles, products of decomposition of the clay mineral, and carbon;
- the precipitation of silicates of complex composition, cristobalite, and Fe₂O₃ particles from eutectic melt;
- the formed porous material is glass ceramics possessing high compressive strength at certain clay/glass/WAS/Fe₂O₃ ratios of in the initial mixtures.

Note, the combination of the mechanical and physical properties of the developed glass ceramics makes it possible to use it not only as brick products, sound- and heat-insulating fillers, but also as a material for immobilization of radioactive wastes.

5. References

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Сажетак: У овом раду, анализирано је формирање фаза у кватернарном систему на температури од 1000°С у ваздуху. У синтерованим смешама је установљено да се порозне керамике састоје из стакласте фазе са јонима гвожђа и кристобалита, силиката које садрже гвожђе, α -Fe₂O₃, и малих количина Fe₃O₄. Порозне стакло керамике поседују тражене захтеве отпорности на притисак и могу се употребити као грађевински материјал.

Кључне речи: црвена глина, WAS (отпадни муљ), Fe₂O₃, синтеровање, стакло керамика.

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