DOI 10.1007/s10717-015-9759-6
Glass and Ceramics, Vol. 72, Nos. 5 – 6, September, 2015 (Russian Original, Nos. 5 – 6, May – June, 2015)

RESOURCE CONSERVATION

UDC 692.232

RESOURCE-CONSERVING TECHNOLOGY OF HEAT-INSULATION-DECORATIVE GLASS-COMPOSITE MATERIAL BASED ON ASH-SLAG WASTES

E. A. Yatsenko,[1, 2] A. P. Zubekhin,[1] V. A. Smolii,[1] I. S. Grushko,[1] A. S. Kosarev,[1] and B. M. Gol'tsman[1]

Translated from *Steklo i Keramika*, No. 6, pp. 34 – 38, June, 2015.

The possibility of producing heat-insulation glass- and glass-ceramic composite construction material based on ash-slag wastes from thermal electric power plants that meets modern construction standards and the physical-mechanical, heat-insulation, and environmental requirements was examined. Compositions and technology for obtaining the constituent parts of heat-insulation-decorative glass-composite material based on ash-slag wastes — cellular heat-insulation glass and slag-sital — with the required physical-chemical properties were developed. The choice of cement binder was substantiated and the mechanism of adhesion between the components of the composite was determined.

Key words: energy conservation, resource conservation, ash-slag wastes from thermal electric power plants, cellular glass, slag sitals, glass-composite material.

One way to solve the problems of energy conservation is to reduce the loss of heat through the building envelope of buildings and structures. It is well known that the ceilings above unheated basements with no light apertures in above-ground walls and above unheated below-ground crawl spaces have the lowest heat-transfer coefficients of the exterior surface of the building envelope (6 W/(m^2 · K)) [1].

Effective exterior thermal insulation with high thermal resistance and mechanical strength that is non-toxic, inflammable, long-lasting, affordable, and easy to install is needed for newly erected and renovated existing buildings. However, most existing thermal insulation does not meet these requirements. In the last few years attention has been increasingly devoted to glass and glass-ceramic composites based on ash-slag wastes, which do not have most of the drawbacks mentioned and can be used as exterior insulation of the facades of residential and commercial buildings and structures [2 – 5]. These materials are distinguished by quite high thermal insulation properties, mechanical strength, and chemical resistance in combination with low production costs.

For this reason it is important to develop compositions and technology for glass and glass-ceramic composite building insulation based on ash-slag wastes from thermal electric power plants.

These investigations followed the structural-logical scheme presented in Fig. 1.

In accordance with the structural-logical scheme presented there are three very important problems involved in the development of heat-insulating glass and glass-ceramic construction ceramic: 1) determination of the optimal composition and technology of porous glass using ash-slag wastes from TPP; 2) determination of the composition and temperature-time regime of synthesis of sital using ash-slag wastes from TPP; 3) development of technology and investigation of the binding of the components of heat-insulating composite. The physical-technical properties of the components of the composite were studied by means of the standard methods and tests.

Glass materials can be synthesized using the ash-slag mixture formed when solid is burned in different thermal

[1] M. I. Platov South-Russian State Polytechnic University (NPI), Novocherkassk, Russia.
[2] E-mail: e_yatsenko@mail.ru.

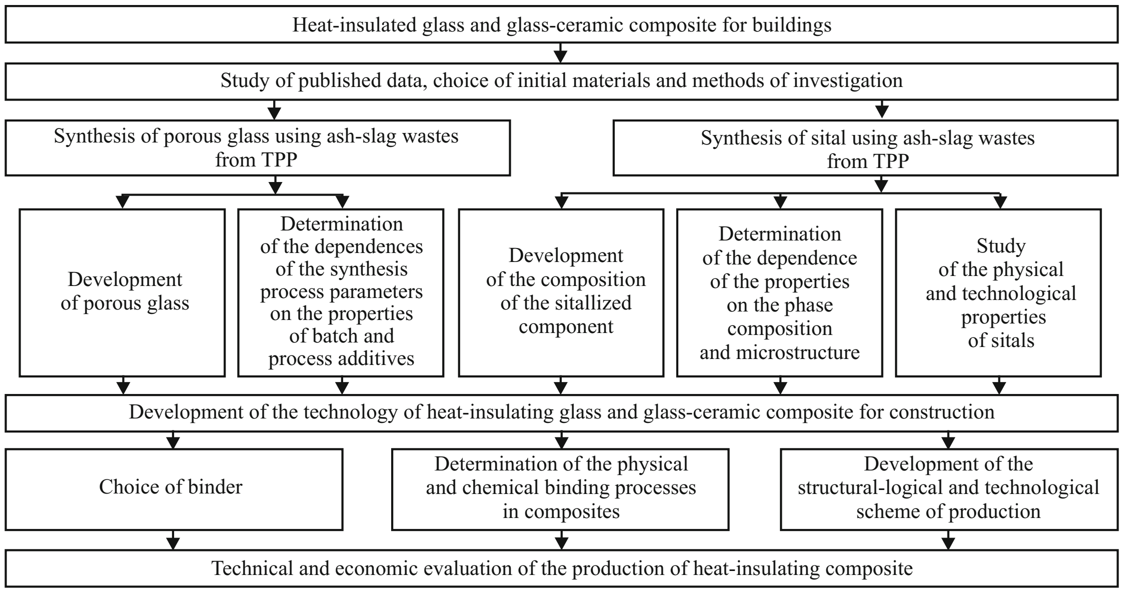

Fig. 1. Structural-logical scheme of the investigations.

power plants. The present investigations were performed on ash-slag wastes from the Novocherkassk regional electric power plant (Table 1).

The composition of porous glass was developed by sintering batch with the following contents (by weight): ash-slag mixture from 10 to 90%[3], cullet from 90 to 10%, borax 5%, and anthracite 5% (above 100%). Sintering was done by the powder method in the temperature interval 800 – 850°C with soaking time 15 – 35 min. Anthracite was used as a pore former, based on the results of previous scientific work [6 – 9].

Considering the need to bring as much ash-slag mixture into production at the lowest sintering temperature the optimal batch composition contains 30% ash-slag mixture with sintering temperature 825°C.

Slag sitals were synthesized on the basis of batch containing 75 – 90% of ash-slag wastes with 5 – 10% added borax, magnesite, zinc white, potassium bichromate, and fluorite. To obtain glass-ceramic materials glass is first obtained at melting temperature 1500°C following [10], which for purposes of sitallization is subjected subsequently to two-step heat-treatment at the established crystallization temperatures of the phases.

Heat-treatment was conducted in the temperature interval extending from 700 to 1000°C in 100°C steps with total soaking time 2 h. Continuous crystallization over the entire volume is secured at temperature 1000°C for all samples, but the sample containing 85% ash-slag wastes, borax, and fluorite is already completely sitallized at 900°C.

[3] Here and below, the content by weight, %.

TABLE 1. Chemical Composition of the Raw Materials

Raw materials	Content, wt.%													
	SiO_2	Al_2O_3	Cr_2O_3	MgO	Na_2O	Fe_2O_3	CaO	K_2O	TiO_2	SO_3	P_2O_5	C	CaF_2	ZnO	LOI
Slag	54.56	19.21	–	1.64	0.98	11.92	3.72	3.35	0.98	0.08	0.12	–	–	–	3.44
Ash	43.30	17.59	–	1.64	0.84	7.60	3.24	3.10	0.82	0.43	0.12	–	–	–	14.8
Ash-slag mixture	56.32	20.08	–	1.43	0.51	11.97	4.02	3.54	0.24	–	0.01	–	–	–	1.53
Cullet	72.94	1.31	–	0.79	15.22	0.25	9.49	–	–	–	–	–	–	–	–
Borax	—	–	34.00	–	14.63	–	–	–	–	–	–	–	–	–	51.37
Magnesite	1.10	–	–	62.70	–	–	0.50	–	–	–	–	–	–	–	35.70
Zinc oxide	–	–	–	–	–	–	–	–	–	–	–	–	–	99.50	–
Fluorspar	2.50	–	–	–	–	–	–	–	–	–	–	–	95.00	–	2.25
Chromium oxide	–	–	99.00	–	–	–	–	–	–	–	–	–	–	–	1.00
Anthracite	–	–	–	–	–	–	–	–	–	–	–	97.00	–	–	3.00
Cement	21.56	5.77	–	0.53	–	4.12	66.24	–	–	0.29	–	–	–	–	–

TABLE 2. Physical and Technical Properties of Samples of Cellular Glass and Slag-Sitals Based on Ash-Slag Wastes from the Novocherkassk Region Power Plant

Sample	Physical and technical properties of the samples						
	Density, g/m^3	Strength in compression, MPa	Strength in bending, MPa	Frost resistance, cycles	Alkali resistance, %	Acid resistance, %	Thermal conductivity, $W/(m \cdot K)$
Cellular glass	200 – 500	1.0 – 5.0	0.2 – 0.5	> 100	75.3	89.9	0.048 – 0.07
Slag-sital	2610	826.1	205.4	> 100	83.1	99.6	1.3 – 1.4

The synthesized components of the heat-insulating-decorative glass-composite material based on ash-slag wastes — cellular glass and slag-sital — must be characterized by a set of properties: ultimate strength in compression and bending; frost resistance; thermal conductivity; and, corrosion resistance (Table 2).

To obtain thermal insulation composites comprised of cellular heat-insulating glass and slag-sital and having the required physical and technical properties it is necessary to have a choice of binders and an acceptable binding technology incorporating surface preparation of the materials, a method of applying the binder, and adherence to the holding parameters (pressure and time).

Portland cement (M500) in the form of a solution of cement : sand (C : S) was used as a binder for the investigations. In addition, according GOST 28013–98 'Construction solutions: General technical conditions', the cement solution consists of C : S = 1 : 3. To increase the cement binder proper, the ratio C : S = 1 : 1 was adopted so as to increase its reactivity by increasing the amount of alite $3CaO \cdot SiO_2$ used.

To determine the mechanism of the reactions occurring in the space between the components of the composite the cement binder is applied in a thin layer and bonding of the binder as a result of adhesion already occurs at this stage.

Adhesion increases on the sital material owing to its ribbing, acquired already at the crystallization stage when the glass is poured into a special mold. However, the surface of the porous glass is rough, which also increases adhesion.

The main physical-chemical process that forms the binding strength of the composite with the use of cement binder is, in our opinion, comprised of the chemical reactions occurring between the silica materials, porous glass, and sital and the products of hydration of cement, which are strongly basic, specifically, the product of hydrolysis $3CaO \cdot SiO_2$ (C_3S) with $Ca(OH)_2$ being released.

According to the data of [11], when Portland cement enters into interaction all of its phases exhibit hydration activity, and as this activity decreases they fall into the following sequence ($3CaO \cdot Al_2O_3 > 4CaO \cdot Al_2O_3 \cdot Fe_2O_3 > 3CaO \cdot SiO_2 > 2CaO \cdot SiO_2$): $C_3A > C_4CaF > C_3S > C_2S$. Tricalcium silicate exhibits with respect to water activity whose degree reaches about 70% C_3S in 20 days. The β-C_2S reaction is slower: only about 30% enters into reaction over 28 days and 90% in one year.

Many investigators have noted that the chemical transformations occurring when cement interacts with water briefly consist in the following [11, 12]. In the reactions of C_3S and β-C_2S with water, calcium hydroxide (CH) — portlandite (calcium hydrosilicates) and amorphized $C_3S(C_2S) + H_2O$ = C-S-H-gel + $Ca(OH)_2$ are formed as products of their hydrolysis.

Subsequently, the silicate components transform into a concrete crystalline state $CaO \cdot SiO_2 \cdot H_2O$. The amount of portlandite $Ca(OH)_2$ can reach 20 – 25% [11[.

Upon hydration at ordinary temperature C_3A forms C_3AH_6, which subsequently transforms into C_4AH_{19}. In the presence of two-phase gypsum (in amount $SO_3 \geq 3.5\%$) C_3A and CSH_2 interact with the formation of ettringite (tricalcium hydrosulfoaluminate):

$$C_3A + 3CSH_2 + 26H = C_6AS_3H_{32},$$

owing to which the cement setting times can be regulated.

In the opinion of A. S. Brykov, calcium aluminoferrites, specifically C_4AF, react with water more slowly than C_3A:

$$C_4AF + CSH_2 + H = C_6(A, F)S_3H_{32}.$$

Thus, the physical-chemical processes of hydration and solidification of the primary clinker minerals of Portland cement (PC) occur. It is necessary to show this in order to give a scientific explanation of the chemical processes occurring between the constituent components.

First, we note the most likely reaction is between portlandite ($Ca(OH)_2$) and SiO_2, which are the predominate components of a block of porous glass and sital tile.

Hydrosilicate with a fine structure forms in the contact layer as a result of this reaction.

The second factor, which can strongly influence the mineralogical composition and structure of the contact layer of the composite, is the presence of the sulfate ion SO_3^{2-} owing to gypsum. Gypsum can interact with C_3A, forming ettringite, which makes it possible to regulate the setting times in cement, as well as forming ettringite in the structure of the contact layer:

$$C_3A + 3CSH_2 + 26H = C_6AS_3H_{32}.$$

Owing to its crystal structure formed during the initial period of hydration ettringite formation is most effective in

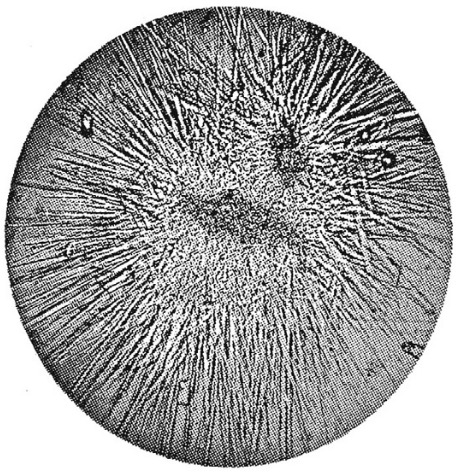

Fig. 2. Ettringite, × 600.

the contact layer. In addition, having a needle structure [13] (Fig. 2), ettringite promotes the formation of a corresponding structure of the contact layer. This gives the composite being developed a high binding strength.

Joining a slag-sital tile and a cellular-glass block using a cement solution with the ratio C : S = 1 : 1 the heat-insulating-decorative glass composite material based on ash-slag wastes acquires initial and final strength at temperature 22°C in 40 min and 72 h, respectively.

In summary, the compositions and technology have been developed for obtaining heat-insulating-decorative glass composite material based on ash-slag wastes and meeting modern building standards and physical-mechanical, heat-insulation, and environmental requirements.

This scientific-research work is part of the Special Federal Program 'Research and development work on priority directions of development of the scientific-technological complex of Russia in 2014 – 2020' of the Ministry of Education and Science of the Russian Federation under contract No. 14.574.21.01.124 providing a subsidy on the theme 'Development of resource-conserving technology of multilayer heat-insulation-decorative glass-composite materials for construction of energy-efficient buildings'. The unique identifier is PHI (project) RFMEFI57414X0124.

REFERENCES

1. V. M. Bondarenko, L. S. Lyakhovich, V. R. Khevchuk, et al., "On normative requirements of thermal protection of buildings," *Stroit. Mater.*, No. 12, 2 – 8 (2001).
2. O. A. Golubchikov, "Heat-insulating building materials," *Sovr. Naukoemkie Tekhnol., Regional'noe Prilozh.*, **24**(4), 72 – 77 (2010).
3. O. V. Kaz'mina, N. A. Kuznetsova, V. I. Vereshchagin, and V. P. Kaz'min, "Production of foam-glass materials based on ash-slag wastes from thermal electric power plants," *Izv. Tomsk. Politekhn. Univ.*, **319**(3), 52 – 56 (2011).
4. A. E. Buruchenko, "Possibilities of using secondary raw material for obtaining construction ceramic and sitals," *Vestn. Tekh. Fiz.-Mat. Nauki*, No. 3, 7 – 14 (2013).
5. D. G. Portnyagin, *Foam-Glass-Ceramic Materials from Compositions of Cullet and High-Calcium Ash-Slag Wastes from Thermal Electric Power Plants, Author's Abstract of Candidate's Thesis* [in Russian], Krasnoyarsk (2012).
6. V. A. Smolii, *Development of Resource-Conserving Technology of Heat-Insulating Cellular Ash-Slag Construction Glass, Author's Abstract of Candidate's Thesis* [in Russian], St. Petersburg (2012).
7. E. A. Yatsenko, V. A. Smolii, A. S. Kosarev, et al., "Physical-chemical properties and structure of foamed slag glass based on thermal power plant wastes," *Steklo Keram.*, No. 1, 3 – 6 (2013); E. A. Yatsenko, V. A. Smolii, A. S. Kosarev, et al., "Physical-chemical properties and structure of foamed slag glass based on thermal power plant wastes," *Glass Ceram.*, **70**(1 – 2), 3 – 6 (2013).
8. E. A. Yatsenko, A. P. Zubekhin, B. M. Gol'tsman, et al., "Investigation of the factors influencing the properties and structure of foamed slag glass," *Steklo Keram.*, No. 4, 3 – 6 (2014); E. A. Yatsenko, A. P. Zubekhin, B. M. Gol'tsman, et al., "Investigation of the factors influencing the properties and structure of foamed slag glass," *Glass Ceram.*, **71**(3 – 4), 111 – 114 (2014).
9. E. A. Yatsenko, V. A. Smolii, B. M. Gol'tsman, and A. S. Kosarev, "Development of compositions and investigation of the properties of block and granular foam glass fabricated using slag wastes from thermal electric power plants," *Izv. Vyssh. Ucheb. Zaved. Sev.-Kavk. Region, Tekh. Nauki*, No. 5, 115 – 119 (2012).
10. *PDF-2: The Powder Diffraction File TM,* International Center for Diffraction Data (ICDD), PDF-2 Release (2012); URL: www.icdd.com (2014).
11. A. S. Brykov, *Silicate Solutions and Their Applications* [in Russian], SPbGTI (TU), St. Petersburg (2009).
12. A. A. Pashchenko, V. P. Serbin, and E. A. Starchevskaya, *Binding Materials* [in Russian], Vishcha shkola, Kiev (1985).
13. T. V. Kuznetsova and S. V. Samchenko, *Microscopy of Materials Used in Cement Production* [in Russian], MIKKhiS, Moscow (2007).