

# THE EFFECT OF CHEMICAL COMPOSITION ON PROPERTIES OF ROCK MELTS

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*The results of investigations of basic physical and chemical properties for aluminosilicate melts of different compositions is presented. It is shown that the highest values of surface tension and adhesion was observed for the basalt melts, whereas neutral aluminosilicate glass melts without iron oxides in their composition are characterized by a high value of contact angle and the lowest values of surface forces. The insertion in the melt of  $ZrO_2$  increases significantly wetting angles, surface tension and adhesion throughout the temperature range as compared with the same melts without zirconia. Basalt melts differ by lower viscosities and significantly less sensitivity to the effects of additives on viscosity of zirconium oxide as compared to the andesite-basalt melts.*

**KEYWORDS:** SILICATE MELT, BASALT, MELTING, WETTING, SURFACE TENSION, ROCK.

## 1. Introduction

Development of the modern industry of the XXI century inseparably linked with wide application of new composite materials on the basis of technical (carbon, glass, high-molecular, mineral, etc.) fibres. The greatest extending to various industries was gained the composite materials and products on the basis of glass fibres, the increase in volume of commodity manufacture in industrially developed countries over the last 5 years makes about 20 % in year. At the same time, these fibres by a complex of physicomaterial and chemical properties, price parameters considerably concede to the new class of mineral fibres - basaltic continuous fibres (BCF). On the basis of BCF a row of new composite materials and products for the industry and special technics is made: rovings and textile twist threads, tapes, cloths and grids, building armature and pipes, various basaltplastic (constructional, electrotechnical, functional, etc.), high-temperature filters for clearing of the heated gases, frictional products and many other things. Basalt fibres are well compatible to polymeric, metal, ceramic, anorganic and carbon matrixes and various fibres at creation hybrid and composite materials. These unique materials in the operating characteristics are surpass analogues from fiber glasses and even steels. They differ durability, reliability, high corrosion durability, are efficient in a wide temperature range (from -260 to 700-900 °C), are chemically inert. Basalt-fibers materials (BFM) are possess high heat- and the sound-proof properties, the raised temperature stability, vibration resistance and durability [1]. They do not generate and do not emit toxic substances, are racks to atmospheric affectings and aggressive environments.

These properties of basalt fibres caused an urgency of a problem of the further development and creation of highly effective building and technical materials and products for various industries, in many cases capable to replace an asbestos, wood, plastic, glass wool and even metal.

Resources of initial basaltic raw materials for manufacture of BFM are inexhaustible and make hundred billions cubic metre. Large supplies of raw materials (rock) for manufacture of basalt fibres, possibility of production of fibres, possessed of a complex high thermalphysic and mechanical properties, are cause an actuality of creation and development of manufacture of wide assortment of new materials and products of technical function on their basis.

However, basalt rocks of various deposits are differ on chemical and mineral composition, therefore for reception of fibres of certain quality correction of conditions of conducting of the basic stages of a process is required. However regular researches of composition - structures - technology - raw materials properties and materials obtained from it has not enough for an estimation for efficiency of use of magmatic rocks of different compositions in production engineering of reception of basalt fibres.

The **purpose** of the present work is to investigate the influence of initial basaltic rocks composition on the basic technological properties of their melts.

## 2. Experimental procedure

As the initial raw materials for manufacturing of fibres from rocks melts of basalt type of different compositions silicate systems with additives zirconium oxide, silica-alumina (neutral) and the alumina-borosilicate glass which chemical compound is resulted in tab. 1 are used.

At manufacturing of fibres from silicate melts quality and productivity of process are appreciably defined by a design and a material of bushing which, as a rule, is produced from platinum-rhodium or other heat-resistant alloys. The optimality of sampling of a draw die material is especially important at manufacturing of fibres from rocks which have narrow interval of fiberizing in comparison with glass fibres [1-4].

In the course of interacting of melt with a material draw die plates it is often enough it diffidence are observed, and in due course trailings of a bushing apertures. Excessive wetting calls fibres thread which leads to a stop of process of a drawing down their fibres and breaks a technological regime.

One of the most important characteristics which define physical parameters of melt interacting with material of the draw die and essentially influence stability of process of fibres reception is wetting which it is characterised by value of wetting angle and surface energy and a surface tension which represent intermolecular and interatomic acts on a surface of substance belongs [5-8]. Considering essential differences of a chemical compound of different kind of raw materials from rocks, research of processes of interacting of base plate with the glasses melts of gained from such rocks, remain the extremely actual.

The evaluation of wetting angle  $\Theta$  (fig. 1) had been carried out with use of direct observations method by indication from the photos gained at the matching temperature on a high-temperature microscope (fig. 1).

Magnitude of a melt surface tension was defined with use of the maximum pressure in a bubble method [9]. The method consists next actions: in the crucible 3 with the melt (fig. 2), which surface tension we define, the calibrated capillary 4 with radius  $r$ , made of chemically inert in relation to material melt (in our case - platinum-rhodium alloy) was entrained. The air with some pressure  $p$  was blown through this capillary.

Numerical value of a surface tension can be defined from dependence [9]:

$$\Delta P_m = \frac{2\sigma}{r} + \rho gh$$

where  $\Delta P_m$  – pressure in a capillary which corresponds to maximum diameter of a bubble;  $g$  – gravitational acceleration;  $\rho$  – melt density;  $h$  – altitude of a melt column over the bottom shearing of a capillary.

Table 1: Chemical composition of raw materials for production of melts

Test number	Rock	Oxides, % (mass)										
		SiO <sub>2</sub>	TiO <sub>2</sub>	ZrO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	FeO	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	B <sub>2</sub> O <sub>3</sub>
1	Silica-alumina glass	73,00	--	--	2,50	--	--	9,50	13,50	1,00	--	--
2	Alumina-borosilicate glass	53,00	--	--	15,00	0,10	--	4,00	17,00	0,20	0,10	10,00
3	Silica-alumina glass from sand	62,9	0,30	--	9,80	0,86	1,57	3,40	17,50	2,00	1,60	--
4	Andezito-basalt	52,84	0,50	--	17,28	8,97	1,66	6,30	7,10	2,20	1,60	--
5	Basalt	49,93	2,50	--	12,63	4,77	9,94	5,45	9,49	2,35	0,85	--
6	Diabase I	48,39	1,72	--	14,25	7,53	1,50	4,80	12,60	3,18	2,32	--
7	Diabase II	43,60	1,29	--	17,42	2,94	9,27	8,65	8,07	3,64	0,73	--
8	Andezito-basalt with ZrO <sub>2</sub> additive	50,20	0,48	5,00	16,42	8,52	1,58	5,99	6,75	2,09	1,52	-
9	Basalt with ZrO <sub>2</sub> additive	44,94	2,25	10,00	11,37	4,29	8,95	4,91	8,54	2,12	0,77	-
10	Basalt with TiO <sub>2</sub> additive	47,55	7,14	-	12,03	4,55	9,46	5,19	9,04	2,24	0,81	-

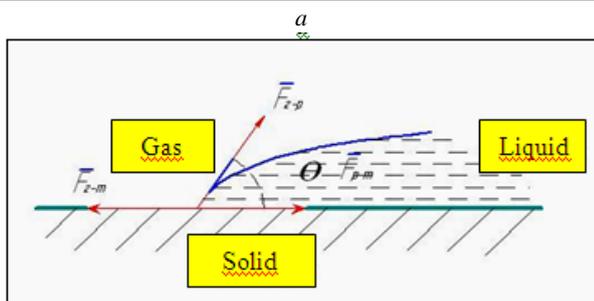
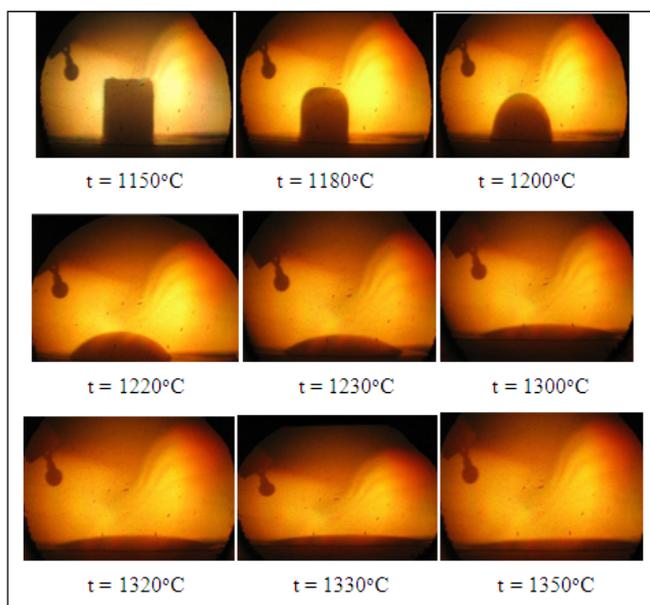


Fig. 1. Deformation of the basalt sample (in the centre) in contact with platinum-rhodium plate at different temperatures (a) and the circuit design of definition of wetting angle  $\theta$  (b)

3. Results and Discussion

On fig. 3 the dependence of a wetting angle of platinum-rhodium base plate carriers by silicate melts of different composition from temperature is presented. Apparently in drawing, melts of silica-alumina neutral glasses in which composition there are no iron joints are characterised by almost stable high value of a wetting angle in a temperature range of existence of liquid phase (melts No. 1 and 2) whereas presence as a part of melt already about 2,5 % iron oxide phases (melt No. 3) essentially reduces wetting angle in all temperature interval of researches and dependence of

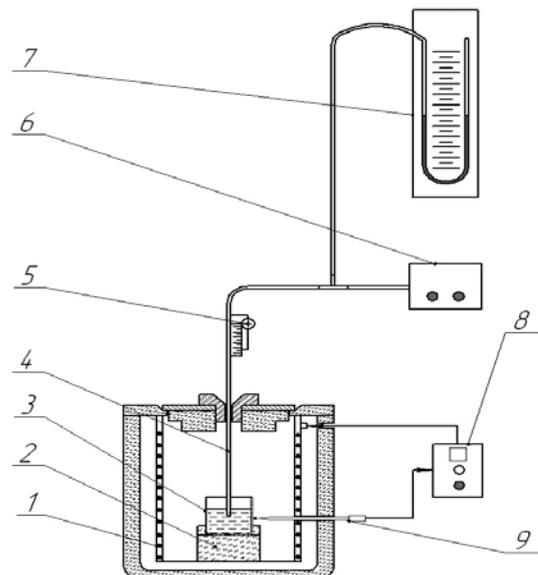


Fig. 2. Apparatus for estimation of melt surface tension: 1 - electric furnace; 2 - jamb; 3 - crucible with melt; 4 - capillary; 5 - micrometric device; 6 - microcompressor; 7 - U-like manometre; 8 - control device; 9 - thermocouple

wetting angle on temperature in comparison with melts 1 and 2 a little increases.

Unlike silica-alumina glasses melts (No. 1-3) wetting angle for soda-lime glasses from rocks of basaltic group which are characterised by presence in the composition up to 15 % (wt.) of iron oxides (melts No. 4, 5, 8, 10) is characterised by already essential dependence on temperature and decreases in 5-6 time at increase in temperature from 1200 °C to 1350 °C. Insertion of 5-10 % ZrO<sub>2</sub> in composition of basalt melts (No. 8 and 9) does not change noted trend, however the general level of values of wetting angles in all temperature range of researches for them is essentially above in comparison with analogous compositions of basaltic melts without zirconium oxide (No. 4 and 5) in all temperature range of researches. Thus, as for the specified initial melts of basaltic group, and for melts with ZrO<sub>2</sub>, value of wetting angles for melts on the basis of andezito-basalt (No. 4 and 8) is exceeded by matching parametres for melts on the basis of basalt (No. 5 and 9).

Essentially smaller values of wetting angles at all temperatures are noted for diabases (melts No. 6 and 7) which contain the least maintenance of SiO<sub>2</sub>.

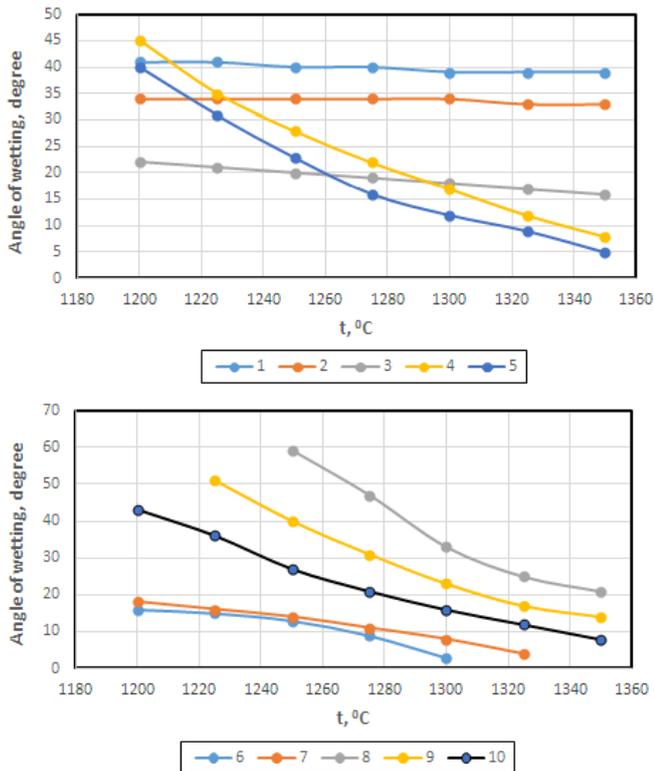


Fig. 3. Relationship between wetting angle by silicate melts of different composition and temperature (curves No. from table 1)

Wetting angles are appreciably defined by surface tension of melt which together with capillary pressure, is one of the basic thermodynamic characteristics of surface layer of liquid on boundary with gas phase and is characterised by intermolecular and interatomic forces on a substance surface. In turn, ability of melt to moisten a solid is defined by a relationship between cohesion of melt and its adhesion to a solid. The specified relationship can be characterised by the value of adhesive tension which is defined as a difference between work of adhesion for a liquid (melt) to a solid body and surface tension on interface liquid-gas. Value of adhesive tension can be defined from dependence [9]:

$$A_H = \sigma_{T-p} \cdot \cos \theta \quad (1)$$

where  $\sigma_{T-p}$  – surface tension on interface of solid - melt;  $\theta$  – wetting angle.

According to results of experimental investigations of silicate melts of different chemical compositions surface tension, the least values of  $\sigma_{T-p}$  in all temperature range belong to silica-alumina glass in which composition iron oxide compounds are virtually absent as well as minimum maintenance of aluminium oxide, however raised contents of  $\text{SiO}_2$  (fig. 4, melt No. 1) that well correlates with high values of wetting angle for this composition of the melt (fig. 4, a). With increase of  $\text{Al}_2\text{O}_3$  content in the melt to 12÷17% (melts No. 5, 6 and 4) the values of surface tension increase too. The maximum values of surface tension is characterized for melts of basaltic group which include 5÷10% of zirconium oxide (melts No. 8 and 9) and a little smaller values  $\sigma_{T-p}$  are noted for andezito-basalt (melt No. 4).

Similar regularity is observed for values of adhesive tension too (fig. 4, b). Yet the character of values  $\sigma_{T-p}$  and  $A_H$  dependences from melt temperature essentially differ: while for the majority of melt compositions with increase in temperature values of surface tension  $\sigma_{T-p}$  decreases, adhesive tension  $A_H$  even slightly increases. That is caused by decrease in wetting angle (fig. 3) and, accordingly, increase for values of  $\cos \theta$  in dependence (1) with increasing of melt temperature.

Thus, similarly to dependence for a wetting angle, utterly insignificant effect of melt temperature on characteristics of surface

and adhesive tension for silica-alumina glasses (melt No. 1) draw attention as well.

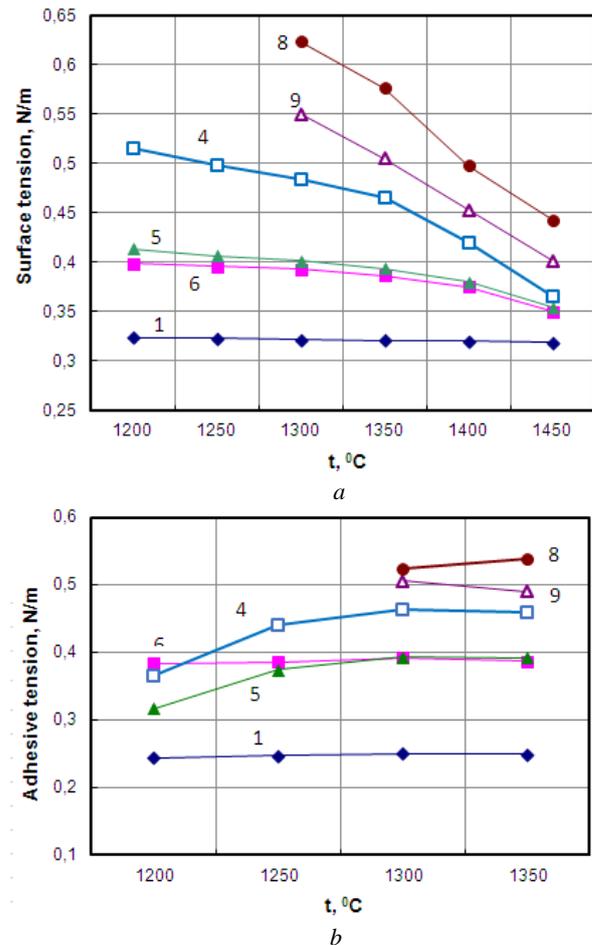


Fig. 4. Relationship between surface (a) and adhesive (b) tension for melts of different composition and temperature (curves No. from table 1)

One of the basic properties for glass-forming melts that characterises an internal friction which arises at moving of one layer of melt in relative to another, is viscosity which appreciably defines possibility of formation of glass fiber. As we can see from fig. 5, injection in the melt composition additives of zirconium oxide leads to essential increase in viscosity for andezito-basalts.

Essentially smaller values of viscosity have the melts of basalt group (fig. 5, b). Thus, considerably smaller effect of zirconium oxide additives on characteristics of basalt melt viscosity in all temperature interval in comparison with andezito-basalt take place.

Important characteristic of rocks melts is speed of fusion which depends on block of processes which lead to production of homogeneous glass mass. Concerning to rocks the speed of fusion is characterised by the parametre of fusibility constant  $K$  which is defined as ratio of refractory oxides mass concentration to that of more fusible oxides [2]:

$$K = \frac{\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{TiO}_2 + \text{FeO} + \text{Fe}_2\text{O}_3}{\text{CaO} + \text{MgO} + \text{Na}_2\text{O} + \text{K}_2\text{O}} \quad (2)$$

With decrease of value of constant fusibility rock is exposed to fusion is easier, therefore for manufacture of fibres mainly use mucks which have  $K < 4,5$  [2]. The estimation of investigated compositions of melts on parametre of constant fusibility (2) shows (fig. 6) that melts of basaltic group (№ 4, 5, 8, 9, 10) (tab. 1) are characterised by the highest values  $K$  that well correlates with the highest values of a surface and adhesive tension (fig. 4) and causes

use for rehash of the specified compositions of rocks of temperature which, as a rule, exceed 1450 °C.

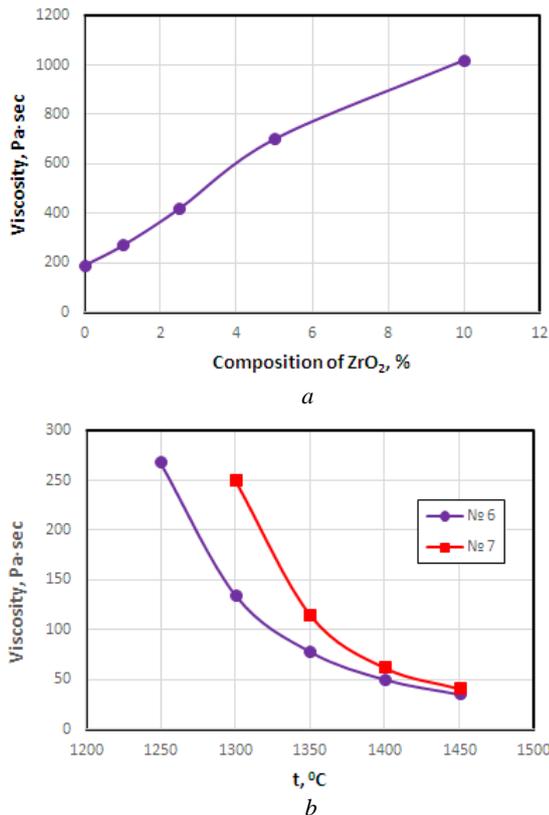


Fig. 5. Relationship between viscosity and content of ZrO<sub>2</sub> in melt of andezito-basalt at 1400 °C (a); viscosity and basalt melt temperature without oxide zirconium (№ 6) and with 10 % ZrO<sub>2</sub> (№ 7, tab. 1) (b)

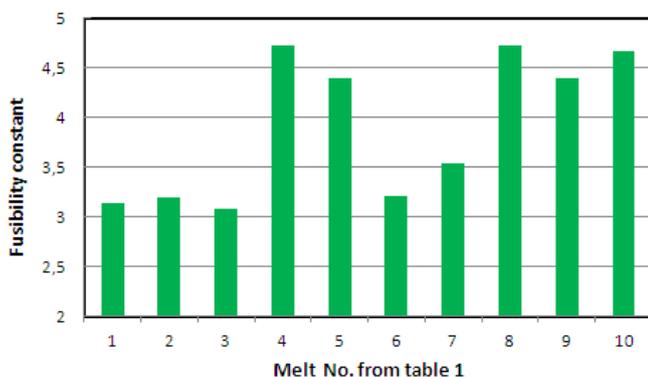


Fig. 6. Value of fusibility constant K for investigated melts

### Conclusions

1. Melts of silica-alumina neutral glasses which have no iron oxides in their composition, are characterised by stably high value of a wetting angles and the least values of surface tension in a temperature range of existence of liquid phase whereas presence as a part of melt already about 2,5 % of iron oxide phases essentially reduces wetting angles in all temperature interval of investigations, and increases dependence of a wetting angles on temperature.

2. Insertion in a basalt melts composition of 5-10 % of ZrO<sub>2</sub> essentially raises the level of magnitudes of wetting angles as well as surface and adhesive tension in all temperature range of investigations in comparison with analogous compositions of basaltic melts without zirconium oxide.

3. Melts of basaltic group are characterised by the highest values of fusibility constant which well correlates with the highest

values of a surface and adhesive tension and causes for their processing use of the specified rocks compositions of temperatures which exceed, as a rule, 1450 °C.

### References

1. Джигирис Д. Д., Махова М. Ф. Основы производства базальтовых волокон и изделий. – М.: Теплоэнергетик, 2002. – 412 с.
2. Углова Т. К., Ходакова Н. Н., Новоселова С. Н., Татаринцева О. С. Переработка тугоплавких горных пород в минеральные волокна // Ползуновский вестник. – 2010. – № 4. – С. 262-265.
3. Новицкий А. Г., Ефремов М. В. Исследование механизма растекания расплава базальта по поверхности фильерных пластин из жаропрочных сплавов при производстве термостойкого волокна // Новые огнеупоры. – 2007. – №2. – С.43-47.
4. Татаринцева О. С., Зимин Д. Е. Особенности плавления горных пород и волокнообразования из расплавов // Ползуновский вестник. – 2006. – №2. – С.158-162.
5. Найдич Ю. В. Контактные явления в металлических расплавах. – К.: Наукова думка. – 1972. – 196 с.
6. Попель С. И. Поверхностные явления в расплавах. – М.: Металлургия, 1994. – 433 с.
7. Vargas S., Frandsen F. J., Dam-Johansen K. Rheological properties of high-temperature melts of coal ashes and other silicates // Progress in Energy and Combustion Science. – 2001. – Vol. 27, Issue 3. – P. 237-429.
8. Прусевич А. А., Кутолин В. А. Поверхностное натяжение магматических расплавов // Геология и геофизика. – Новосибирск: Наука. – 1986. – С. 58-67.
9. Справочник химика 21. Химия и химическая технология // <http://chem21.info>.