Peculiarities of the use of siliceous raw materials of the Russian Far East in the integrated pipeline protection

Elena A. Yatsenko[1], Boris M. Goltsman[1,a], Anna V. Ryabova[1] and Victoria A. Smoliy[1]

[1]*Platov South-Russian State Polytechnic University (NPI), 346428 Novocherkassk, Russia*

Abstract. Modern trends in the development of Russian oil and gas infrastructure are examined. The important role of the Far East in the transportation and export of oil is revealed. The main threats in the operation of pipelines are described. The integrated protection technology of pipeline surfaces is proposed. The structure and properties of local silicate raw material – diatomite – are studied. The technology of obtaining glass enamel coating is designed to protect the internal surface of the pipe. The phase composition, microstructure and properties of the coating are compared with analogues. The technology of foam glass production is designed to protect the external surface of the pipe. The foaming processes are studied; the properties and structure of the material are examined. The optimum ratio of raw materials is revealed. Recommendations on the application of the developed technology for integrated pipeline protection are given.

1 Introduction

Currently, the main sources of energy are oil, natural gas and coal. Oil fuel due to the convenience of its transportation is the most valuable for vehicles, which are the main oil consumers. Over the past 20 years, world energy consumption has increased by 30%, and this growth is likely to continue due to the growing demand of the rapidly developing countries of the Asian region.

The energy industry is one of the most important structural components of the Russian economy. The main center of new industrial development is the Far East [1], which performs an important transit function. There is an export of oil through its territory from other regions of the country, first of all – from Siberia. In addition, it borders with China, which is one of the largest consumers of Russian hydrocarbons.

Transportation of oil and gas is carried out through steel pipelines of various diameters and assortments. The safety of pipeline operation strongly depends on the quality of the corrosion protection. Corrosion elements represent a particular danger as a source and amplifier of a wandering direct current, which leads to a perforating destruction of the metal contacting with the electrically conductive aggressive medium. The aggressive impact on the pipe wall is caused by oil from the inside and the soil from the outside. Internal protection is designed to counteract corrosion of pipes under the influence of a transported aggressive medium, and to reduce the hydraulic resistance of pipelines and increase their throughput. External protection is designed not only to maintain the integrity of pipes, the quality of oil products and the speed of their transportation, but also to protect human health and the environment. Therefore, additional requirements are imposed to external protection: prevention of condensation and high temperatures on the surface of the pipe; elimination of noise generated by pressure drop inside the pipe; prevention of temperature losses leading to solidification of transported oil; minimal impact on the environment.

The most reliable and versatile materials for the protection of pipelines are silicate materials, that can be used for manufacturing of a wide range of materials and coatings. Silicate-enamel coatings are the most promising for internal protection, due to their high chemical, thermal, corrosion and abrasion resistance. They also do not allow deposits on the pipe walls, reliably operate at temperatures from -50 to +350 ° C and provide anticorrosion protection of pipelines for at least 50 years.

The only material eligible for the external protection is foam glass – a thermal insulating material, which is literally a foamed glass mass. Along with excellent thermal insulation properties and full ecological, fire and hygienic safety, foam glass has the following range of properties: durability, incombustibility, ease of handling and installation, stability, resistance to atmospheric and biological effects, etc. In addition, foam glass materials can be obtained on the basis of a wide range of raw materials [1-7].

It is important to note that any large-scale production requires a local raw material base. The possibility of using amorphous raw materials in both silicate enamel technology [8-9] and foam glass technology [10-13] has been confirmed by a number of studies. Therefore, the presence of extensive deposits of amorphous silica [14] and silica-bearing rocks in Eastern Siberia and the Far

[a] Corresponding author: boriuspost@gmail.com

East, as well as the possibility of synthesizing amorphous silica from quartz-containing raw materials [15] makes it possible and necessary to develop the proposed technology for integrated protection of pipelines in the evolving network of oil and gas pipelines of the Russian Far East.

2 Materials and Methods

The main criteria of raw material selection for the study were the maximum amount of silicon oxide and the minimum content of impurities. The following raw materials were chosen: the diatomite of the Chernoyarsky deposit and the quartz sand of the Chalgan deposit. All deposits are located in the Khabarovsk Territory in a small distance from the cities and the nearest passage of oil pipelines. The chemical composition of the selected raw materials is given in Table 1.

Table 1. Chemical composition of raw materials.

Material	Chemical composition, [wt. %]					
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Calci-nation losses
Diatomite	76,2	6,8	3,5	1,0	0,9	11,6
Quartz sand	99,7	–	0,02	–	–	0,3

Enamel frits were vitrified in alundum crucibles in an electric furnace at a temperature of 1100-1350 °C with an exposure of 1 h [16-17]. Cooling of the melt was carried out by granulation in cold water. The frits milled to 63 μm fraction (mesh No. 230) and then used to prepare slurry suspension consisting additionally: water – 40 %, refractory clay – 4 %, electrolyte – 0,1 %. The slurry was applied to 1008 steel samples using the dipping method. The excess slurry was removed, and then the samples were dried for 15 minutes at a temperature of 75-100 °C. Then the samples were fired in an electric furnace at a temperature of 850 °C with an exposure time of 3 min.

The softening point and flowability were determined on pressed cylindrical samples of a frit. The samples were heated and sequentially extracted from the furnace after each 10 °C to determine the softening point. The temperature at which the melting (decreasing the height) of the sample begins is the softening point. To determine flowability, the samples were placed on prepared steel plates, heated up to 850 °C, held for 2 minutes, sharply tilted to an angle of 45 °, followed by holding for 2 minutes. After cooling, the length of the sample was measured.

Temperature coefficient of linear expansion (TCLE) of enamel was determined on a vertical dilatometer DKV-4 in the temperature range 50-400 °C by measuring the relative elongation of the sample upon heating (Eq. 1):

$$\alpha = (\Delta t \cdot \Delta l \cdot 10^{-3} / l_0) + \alpha_q \quad (1)$$

where α – TCLE; Δt – temperature difference, °C; Δl – sample elongation, mm; l_0 – initial sample length, mm; $\alpha_q = 5{,}5 \cdot 10^{-7}$ °C^{-1} – TCLE of quartz glass.

Production of foam glass was conducted by the standard powder method. Raw materials (glass cullet, diatomite) were pre-dried at 120 °C. The resulting dry powders were milled to 210 μm fraction (mesh No. 70). Foaming mixture was prepared in a separate vessel by mixing the components (waterglass, glycerol, water) in a given proportion. Afterwards, the prepared raw materials were composed, mixed and molded into cubes with edge length of 20 mm and mass of 10 g (volume $8 \cdot 10^{-6}$ m^3, density 1250 kg/m^3). Then samples were loaded into a furnace for heat treatment according to [18-20].

When the air inside the furnace cooled to room temperature, the samples were removed from the furnace and subjected to mechanical processing (filing) to give them a regular shape. Further, the weight of the samples of given shape was measured. Then calculations of the volume *(V, cm^3)*, apparent density *(D, kg/m^3)* and foaming coefficient (*FC)* were performed based on the obtained data according to Eq. 2 – Eq. 4, respectively.

$$V = a \cdot b \cdot c \quad (2)$$

$$D = m / V \cdot 1000 \quad (3)$$

$$FC = V / 8 \quad (4)$$

where *a* – sample length, cm; *b* – sample width, cm; *c* – sample height, cm; *V* – sample volume, cm^3; m – sample mass, g.

Each recorded testing value was the mean of the results from five samples.

Analysis of the sample microstructure was performed on a TEScan VEGA II LMU scanning electron microscope with INCA ENERGY 450/XT energy dispersive microanalysis (Silicon Drift (ADD) detector). Samples were placed on a conductive carbon tape; the surface is deposited with carbon. The differential thermal analysis was carried out on a STA 449 Jupiter device in platinum crucibles with a cover. Measurement mode: temperature range 30-1000 ° C; heating rate (10 °C/min); medium: air. X-ray phase analysis was performed on a diffractometer "DRON-7". Measurement mode: scanning range 10.00-90.00 °; scanning method 2THETA-THETA; exposure 1 sec; step 0,050 °; radiation of Cu (29); wavelength 1.5406 Å.

3 Results and discussion

An X-ray phase analysis was performed for a preliminary assessment of the possibility of using diatomite as raw material to produce silicate materials, shown in Figure 1.

It can be seen that the diatomite is composed of an amorphous substance with crystalline formations consisting of various modifications of SiO_2 (mostly, β-quartz) and small quantity of $(Al_2O_3)_m \cdot (SiO_2)_n$ minerals. To study the features of phase and structural transformations during the heat treatment process, a differential thermal analysis was performed, its results are shown in Figure 2.

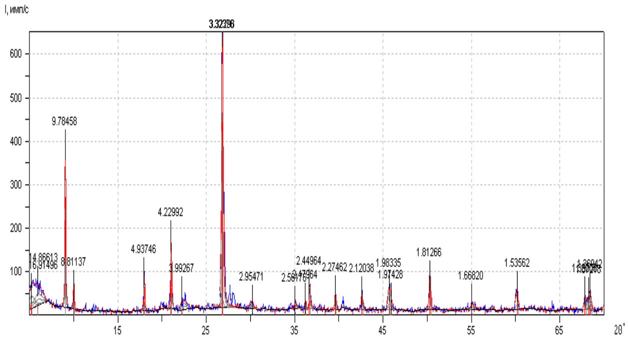

Figure 1. Results of X-ray phase analysis of diatomite.

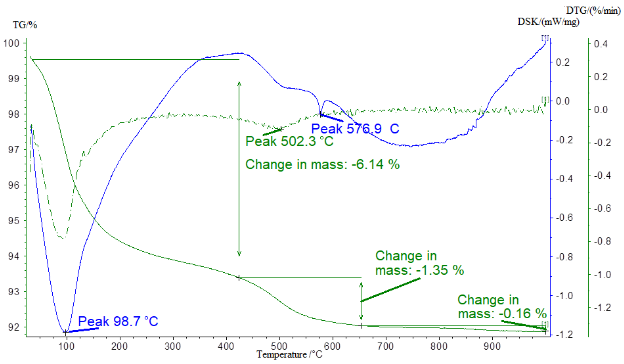

Figure 2. Results of differential thermal analysis of diatomite.

The presence of the endothermic effect in the temperature range up to 200 °C on the DTA curves indicates the removal of adsorption water, which is confirmed by indicating its smooth continuous dehydration during heating up to 1000 °C, with the main part of the water being already removed before 425 °C. The appearance of an endothermic effect on the curve with a minimum at 577 °C is due to the polymorphous transformation of crystalline quartz.

3.1. Glass enamel coating

Three glass compositions in the system «R_2O – RO – SiO_2 – Al_2O_3 – B_2O_3 –TiO_2 – CaF_2 – Na_3AlF_6 – Fe_2O_3 – Co_2O_3» were synthesized to study the diatomite suitability for the enameling of steel pipelines. In these compositions, the raw material for the introduction of silicon oxide SiO_2 was changed: in the A1 composition it was introduced by chemically pure raw material – silicon hydrate $SiO_2 \cdot nH_2O$, in the A2 composition – by quartz sand, in A3 – by partial replacement of quartz sand with diatomite.

During melting, it was found that the processes of glass formation occur more intensively and at a lower temperature in composition A3 (synthesis mode 1100 °C, 5 hours), while compositions A1 and A2 were synthesized at 1350 °C, 7 hours. It can be explained by the fact that in compositions A1 and A2 silica is introduced by crystalline compounds – silicon hydrate and sand, which are characterized by a higher structural strength. At the same time in composition A3 most of the silica is introduced by its amorphous form. Then X-ray phase analysis of coatings was performed to study their phase composition, the results are shown in Figure3.

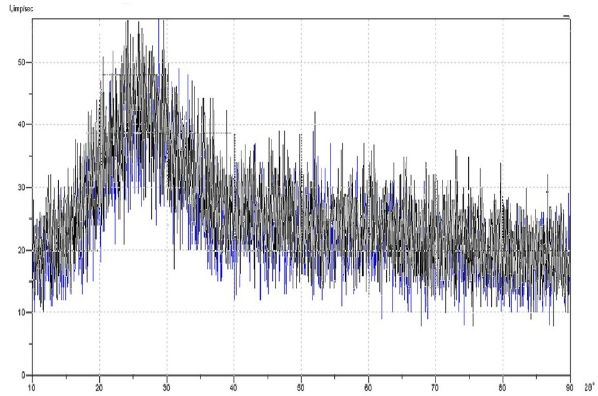

Figure 3. X-ray patterns of glass enamels: black – A1 composition, gray – A2 composition, blue – A3 composition.

Obtained results show that all coatings are in an amorphous state and do not have pronounced peaks, which indicates a homogeneous structure of the coatings. Technological properties of synthesized enamel frits (determined experimentally) are presented in Table 2.

Table 2. Technological properties of the A series samples.

Composition	TCLE at 400 °C, [°C^{-1}·10^{-7}]	Softening point, [°C]	Flowability, [mm]
A1	105,07	510	47
A2	107,32	480	46
A3	103,69	450	49

The obtained results show that all synthesized frits are characterized by similar characteristics and enter the intervals permissible for silicate enamel coatings. However, a comparative analysis shows that partial replacement of silicon hydrate and quartz sand with diatomite significantly reduces melting temperature and the viscosity of glass melt. In addition, the frit obtained with amorphous silica is characterized by greater flowability, which will contribute to a better uniform formation of the enamel coating These observations are confirmed by the results of a study of the microstructure of the coatings (Figure 4).

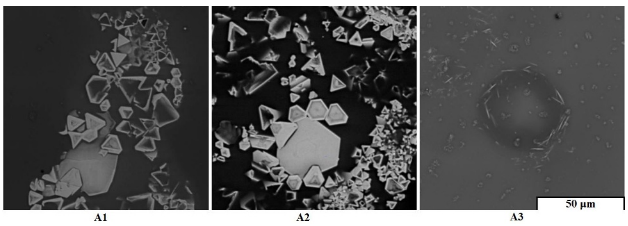

Figure 4. Microstructure of glass enamel coatings A1-A3.

The amorphous vitreous phase in the photographs is represented by dark areas, and the crystalline phase in the form of crystals of different size. It can be seen that the structure of the coating is most uniform in A3 composition based on diatomite. In samples of other compositions, crystalline inclusions of various sizes and geometric shapes were observed. Thus, partial or complete replacement of quartz sand with amorphous silica materials, in particular diatomite, reduces the duration of the silicate and glass formation by 30 % and reduces energy consumption due to the reduction of the maximum temperature by 200 °C.

3.2 Foam glass

According to the obtained results, a number of compositions of the B series were developed to study the possibility of using silicate raw materials of the Far East in the production of foam glass. The compositions include the following raw materials: colorless glass cullet, diatomite of the Chernoyarsky deposit. The ratio of materials is shown in Table 3. The pore-forming mixture was introduced in an amount of 10 wt. % over 100.

Table 3. Technological properties of the A series samples.

Component	Component content, wt.%, in composition, #				
	B1	B2	B3	B4	B5
Diatomite	20	40	60	80	100
Glass cullet	80	60	40	20	0

Samples of the B series were heat-treated at the foaming temperatures 800, 850, 900 °C. The structure of the samples obtained at 850 °C is shown in Figure 5, the properties of the samples are shown in Table 4.

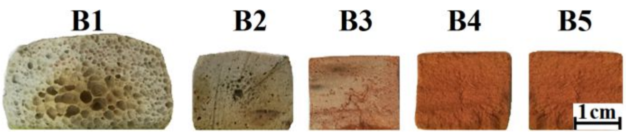

Figure 5. Internal structure of B series samples (foaming temperature 850 °C).

Table 3. Technological properties of the A series samples.

	B1	B2	B3	B4	B5
Foaming temperature 800 °C					
Density, [kg/m^3]	385,25	950,37	1401,87	952,05	941,74
Foaming coefficient	2,81	1,20	0,81	1,08	1,05
Foaming temperature 850 °C					
Density, [kg/m^3]	235,62	769,07	1633,85	1135,67	1135,09
Foaming coefficient	3,82	1,36	0,66	0,91	0,82
Foaming temperature 900 °C					
Density, [kg/m^3]	211,30	723,17	1627,29	1113,85	1243,18
Foaming coefficient	3,53	1,53	0,61	0,85	0,70

It should be noted that during the thermal processing of silicate materials, the sintering and melting processes are carried out successively. In the case of foam glass, sintering is accompanied by a decrease in volume due to the contraction of the batch particles, and melting is accompanied by an increase in volume due to foaming of the softened glass mass with gases from the foaming agent. The results obtained demonstrate that introduction of 20 wt. % of diatomite (B1) allows to obtain foam glass with a density of about 200 kg/m^3. Then foaming noticeably deteriorates with the addition of 40 wt. % of diatomite (B2), and the density increases to 700 kg/m^3. Composition B3 with 60 wt. % of diatomite has the highest density among all of the samples because of intense sintering, but its viscosity does not allow the pore formation. In compositions B4 and B5, both foaming and sintering processes are absent.

For the foaming of compositions B3-B5, it is necessary to introduce flux additives which intensifying the sintering and melting of the material. Therefore, the flux (NaF) in an amount of 10 wt. % over 100 was added in the samples of composition B3-B5 (compositions B3*-B5*, respectively). The samples were subjected to heat treatment at foaming temperatures of 800, 850, 900 ° C. Structure of the obtained samples are shown in Fig. 6, comparison of the phase composition of samples B1 and B5* - in Figure 7.

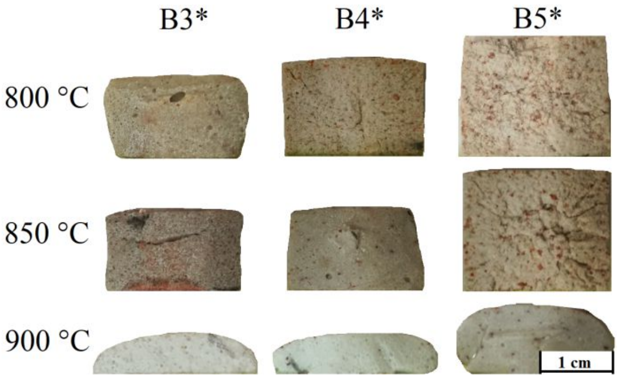

Figure 6. Internal structure of B* series samples, modified with flux.

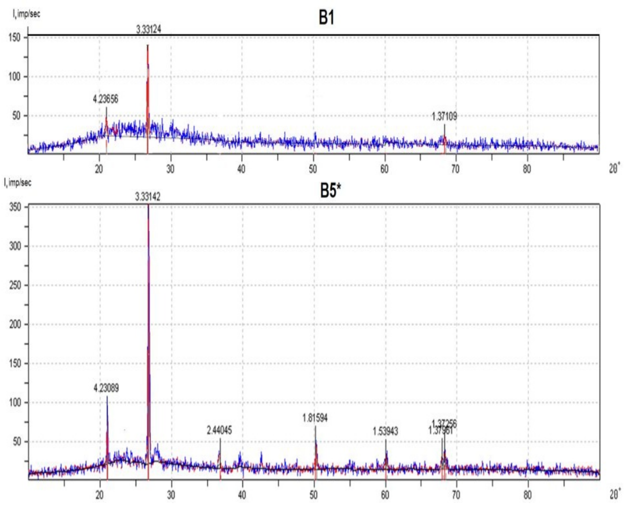

Figure 7. Results of X-ray phase analysis of foam glass

Comparing the samples of the B and the B* series, it can be seen that the introduction of then flux significantly accelerated the melting process. In this case, the presence of more diatomite in the composition led to an increase in the amount of the crystalline phase (β-quartz). Also, the intensity of pore formation decreased, which required the introduction of additives that enhance gas generation.

4 Summary

The possibility of using silicate raw materials of the Far East in the production of glass materials for steel pipeline protection was investigated. It was found that diatomite is more eligible for obtaining enamels than traditional raw materials (quartz sands). Coatings based on diatomite can be obtained at lower temperature, have all required properties and uniform defect-free structure. The use of diatomite in the production of foam glass is complicated by its high melting point, the maximum possible amount of diatomite is 20 wt. %. To introduce a larger amount, additional introduction of intensifying additives is required. With their use, up to 80% diatomite can be used in foam glass.

The use of developed materials will significantly increase the service life of pipelines, reduce the cost of their maintenance, and reduce environmental risks in the surrounding areas. The use of local raw materials will allow the introduction of the proposed technology for integrated pipeline protection at the branch enterprises of the Far East of Russia.

5 Acknowledgements

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