AGREGADO LEVE E CONCRETO A BASE DE ESCÓRIAS, COM ALTO CONTEÚDO RESIDUAL DE COMBUSTÍVEL

LIGHTWEIGHT AGGREGATE AND ASHES SLAG BASED CONCRETE WITH HIGH RESIDUAL FUEL CONTENT

ЛЕГКИЙ ЗАПОЛНИТЕЛЬ И БЕТОН НА ОСНОВЕ ЗОЛОШЛАКА С ВЫСОКИМ СОДЕРЖАНИЕМ ОСТАТОЧНОГО ТОПЛИВА

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RESUMO

Os materiais de escória de cinzas na composição química e mineralógica são em grande parte idênticos às matérias-primas minerais naturais. Eles são uma fonte de poluição ambiental, representam uma ameaça à saúde pública e uma ameaça à flora e fauna das áreas circundantes. O desperdício de cinzas de escória contém uma grande quantidade de combustível não queimado. Em algumas cinzas, o teor de combustível não queimado pode representar de 20 a 40%. Nesse caso, é aconselhável usá-lo como matéria-prima para a produção de agregados porosos artificiais. O artigo apresenta os resultados de estudos sobre o desenvolvimento de tecnologia de agregados leves baseados em escória de cinzas com alto teor de combustível residual. Para desenvolver a tecnologia do agregado leve, a escória de cinzas foi usada pela Nova Zinc LLP (região de Karaganda, Cazaquistão), na qual o teor de carvão não queimado é de até 75%. Com base na escória de cinzas, foram obtidos agregados leves usando tecnologias de queima e não queima. Pela tecnologia de torrefação (queima), os agregados foram obtidos queimando a uma temperatura de 1000 e 1100 °C. Os agregados obtidos têm uma densidade aparente de 395-687 kg/m³ e uma resistência à compressão no cilindro de 0,5-2,4 MPa. Por tecnologia não queima, o cimento Portland M400 foi usado como adstringente. Após o endurecimento, os agregados têm uma densidade aparente de 400-600 kg/m³ e uma resistência à compressão de 0,65-1,5 MPa no cilindro. Amostras de concreto leve com densidade de 1200 e 1700 kg/m³, resistência à compressão de 80 (B5) e 120 kg/cm² (B7,5) e coeficientes de condutividade térmica de 0,43 e 0,67 W/m·°C com base no agregado leve não queimado, respectivamente. O agregado leve e o concreto leve em suas propriedades funcionais atendem aos requisitos dos documentos regulamentares.

Palavras-chave: tecnologia de queima, temperatura, tecnologia de clínquer, fichário, endurecimento, densidade aparente, resistência.

ABSTRACT

Ashes slag materials in the chemical and mineralogical composition are largely identical to natural mineral raw materials. They are a source of environmental pollution, pose a threat to public health, and a threat to the flora and fauna of the surrounding areas. Ashes slag waste contains a large amount of unburned fuel. In some ashes, the content of unburned fuel can reach 20-40%. In this case, it is advisable to use it as a raw material for the production of artificial porous aggregates. The paper presents the results of studies on the development of lightweight aggregate technology based on ashes slag with a high residual fuel content. To develop the technology of lightweight aggregate, ashes slag was used by Nova Zinc LLP (Karaganda region, Kazakhstan), in which the content of unburned coal is up to 75%. Based on ashes slag, lightweight aggregates were obtained using burning and non-burning technologies. By roasting (burning) technology, aggregates were obtained by burning at a temperature of 1000 and 1100 °C. The aggregates obtained have a bulk density of 395-687 kg/m³ and a compressive strength in the cylinder of 0.5-2.4 MPa. By non-burning technology Portland cement M400 was used as an astringent. After hardening, the aggregates have a bulk density of 400-600 kg/m³ and a

compressive strength of 0.65-1.5 MPa in the cylinder. Samples of light concrete with a density of 1200 and 1700 kg/m³, a compressive strength of 80 (B5) and 120 kg/cm² (B7.5), and thermal conductivity coefficients of 0.43 and 0.67 W/m·°C were obtained on the basis of the non-fired light aggregate, respectively. Lightweight aggregate and lightweight concrete in their functional properties meet the requirements of regulatory documents.

Keywords: *burning technology, temperature, clinker technology, binder, hardening, bulk density, strength.*

АБСТРАКТ

Золошлаковые материалы по химическому и минералогическому составу во многом идентичны природному минеральному сырью. Они являются источником загрязнения окружающей среды, представляют опасность для здоровья населения и угрозу растительному и животному миру близлежащих районов. Золошлаковые отходы содержат в своем составе большое количество несгоревшего топлива. В некоторых золах содержание несгоревшего топлива может достигать 20-40%. В этом случае ее целесообразно применять как сырье для производства искусственных пористых заполнителей. В статье приведены результаты исследований по разработке технологии легкого заполнителя на основе золошлака с высоким содержанием остаточного топлива. Для разработки технологии легкого заполнителя применялся золошлак ТОО «Nova Цинк» (Карагандинская обл., Казахстан), в котором содержание несгоревшего угля составляет до 75%. На основе золошлака получены легкие заполнители по обжиговой и безобжиговой технологиям. По обжиговой технологии заполнители получали обжигом при температуре 1000 и 1100 °C. Полученные заполнители имеют насыпную плотность 395-687 кг/м³ и прочность при сдавливании в цилиндре 0,5-2,4 МПа. По безобжиговой технологии в качестве вяжущего компонента применялся портландцемент М 400. После твердения заполнители имеют насыпную плотность 400-600 кг/м³ и прочность при сдавливании в цилиндре 0,65-1,5 МПа. На основе безобжигового легкого заполнителя получены образцы легких бетонов с плотностью 1200 и 1700 кг/м³, прочностью на сжатие 80 (B5) и 120 кг/см² (B7.5) и коэффициентами теплопроводности 0,43 и 0,67 Вт/м·°C, соответственно. Легкий заполнитель и легкие бетоны по своим функциональным свойствам отвечают требованиям нормативных документов.

Ключевые слова: *обжиговая технология, температура, клинкерная технология, вяжущее, твердение, насыпная плотность, прочность.*

INTRODUCTION

Ashes slag materials in the chemical and mineralogical composition are largely identical to natural mineral raw materials. The level of disposal of this waste in Russia is about 4-5%; in a number of developed countries - about 50%, in France and Germany - 70%, and in Finland - about 90% of their current output. Dry ash is mainly used in these countries, and government policies are being pursued to encourage their use. So, in Poland, the price of land for ash dumps is sharply increased. Therefore, thermal power plants pay extra to consumers in order to reduce their own costs for their storage. In China, ash is delivered to consumers free of charge, while in Bulgaria ash itself is free. In the UK, there are five regional centers for the sale of ashes (Putilin, 2003).

The content of ashes slag material dumps requires high operating costs, which affect the increase in the cost of energy production. They are a source of environmental pollution, pose a threat to public health, and a threat to flora and

fauna of the surrounding areas. Of particular danger are ash dumps located near water basins (rivers and lakes), due to the possible breakthrough of dams. The essential argument against the construction of new fuel power stations (FPS) is often the need to create ash dumps near them. Their use in industry, the construction industry, and agriculture is one of the strategic ways to solve the environmental problem in the zone of FPS operation. Therefore, the development of building materials technology using ash and slag is an urgent task.

The purpose of this study is to develop lightweight aggregate technology and concrete based on ashes slag (AS) with a high content of residual fuel.

One of the first in world practice, American researchers began to use ash for the production of bricks (Antipin, 1969; Reidelbachl, 1970). The American company "TekoledyCorp" developed brick compositions from various industrial wastes such as ash, foundry sands, asbestos wastes, furnace slags (Suleimenov, 2004).

The author of (Malykhin, 2019) conducted experiments to strengthen clay soils using an ash-slag mixture of Novokemerovskaya fuel power center (FPC) and cement M400 CEMII/A-Sh 32.5B of the Topkinsk plant. The greatest water resistance and durability in a water-saturated state are possessed by samples reinforced with 25% AS and 15% cement.

Every year, 3.1 million tons of cement are replaced annually in Germany by A&S dumps. Thanks to this, the resources and energy necessary for the production of cement are saved, and the costs of silos, transportation, and wages are paid back (Malykhin, 2019).

South Africa, with financial state support, is carrying out experimental construction of routes from fly ash (Brooks, 2009). It is proved that mixtures of fly ash with inert materials (sand, rice husk, etc.) reach from 50 to 70% of the strength of materials reinforced with cement.

The American Coal Ash Association and the Municipal Solid Waste Management Group co-sponsor the Coal Firing Partnership. The project is intended to help construction organizations and energy companies understand the environmental benefits and potential consequences of using coal combustion products for various purposes, as well as stimulate their useful use (Lindon, 2015).

Currently, domestic and near-abroad scientists conduct research on the development of compositions and technology of lightweight aggregates, concrete, mortars, and ceramic bricks using ash and slag waste (Maximov, 2004; Denisov, 2008; Turkina, 2009; Gilyazidinova, 2010; Montaeva, 2012; Maksakov, 2012; Lokhova, 2012; Mestnikov, 2013; Abramov, 2013; Netesa, 2013; Malchik, 2015; Kadyrbekov, 2016; Malchik, 2016; Dmitriev, 2017). So, at the Jurgen Institute of Technology (Malchik, 2016), research was conducted on the use of AS in brick production. The optimal percentage ratio for adding ash and slag waste is 15%, at a burning temperature of 1000 °C. In this case, the compressive strength of the samples is 125 kg/cm² without ash and 110 kg/cm² with ash. The thermal conductivity of samples without ash is 0.85 W/m·°C, with ash - 0.76 W/m·°C.

In (Dmitriev, 2017), the introduction of AS waste and rice husk ash into a gas concrete mixture was proposed, which allows to increase the strength, crack resistance of aerated concrete by hardening and compaction of concrete due to the higher particle density. This increases the resistance of aerated concrete to high

temperatures, that is, increase its fire resistance.

MATERIALS AND METHODS

As the main raw material used AS of the enterprise LLP "Nova Zinc" (Karaganda region, Kazakhstan).

For the manufacture of lightweight aggregate by roasting (burning) technology, local loam and highly plastic bentonite clay were used.

For the manufacture of lightweight aggregate by non-firing technology, Portland cement CEM I 32.5 H (Government standard - GOST 31108-2003), gypsum, and liquid glass corresponding to GOST 13078-81 were used as a binder. To accelerate the setting time of cement concrete, calcium chloride (CaCl₂) was used.

To make mixtures, the ashes slags was dried in an oven at a temperature of 100-110 °C to a residual moisture content of 3-4% and then subjected to grinding in a laboratory ball mill until it passes through a 1.25 sieve.

When compiling clay-ash-slag mixtures, the dried clay was crushed and sieved through a sieve of 0.63. To obtain aggregate granules, ash and clay were mixed in certain proportions, and then the mixture was moistened with water until a formable mass was obtained, from which granules with a diameter of 10-20 mm were made using a laboratory granulator. After drying at a temperature from 100 to 105 °C for 1 to 2 hours in an oven, the pellets were fired in a SNOL 1.6 / 1300 muffle furnace at temperatures of 900, 1000, and 1100 °C for 1 hour. After that, their density and strength were determined. In the preparation of clinker-based mixtures, AS were mixed with Portland cement in certain proportions, then the mixture was moistened with water to obtain a workable mixture, from which granules with a diameter of 10-20 mm were also made. Hardening accelerators were added to the mixture along with mixing water. After molding, the granules were kept in a humid environment for 7 and 14 days. After that, their density and strength were determined.

X-ray phase analysis (X-ray PA) was carried out on a DRON-3M diffractometer using C system-K α radiation. The sensitivity of the methods is from 1% to 2%. X-ray PA powder diffraction samples were subjected to passing through a sieve of 100 holes/mm. Radiographs were identified using reference data (Mikheev, 1957).

Differential thermal analysis (DTA) was carried

out on a "Deridalograf" Q-1500 D instrument of the Paulik and Erden system (Hungary) at a temperature change of 7.5 and 10 deg/min.

The physical-mechanical properties of the lightweight aggregate were determined by the method (GOST 9758-2012). The physical-mechanical properties of lightweight concrete were determined by the method (GOST 25820-2014). The thermal conductivity of lightweight concrete was determined using an ITP MG4 100 device.

3. RESULTS AND DISCUSSION

In the technical conditions for the use of ash from FPS as a fine aggregate for structural heat-insulating lightweight concrete (Technical conditions TC-21-33-1-73), the requirements for the grain composition and content of harmful impurities are given. In particular, fuel residues in ash obtained from burning brown coal are allowed no more than 5%, and from burning coal and anthracite up to 12% (by weight). Often in ashes, there is more unburned fuel - up to 20-40%. At the same time, the possibilities of using ash as a filler are limited, especially for reinforced structures. In this case, it is advisable to use it as a raw material for the production of artificial porous aggregates. The maximum permissible content of fuel residues in the ash, suitable for the production of alumina expanded clay, should not exceed 17%. At the excess amount of carbon, the granules melt, and the quality of the aggregate deteriorates (Dvorkin, 2007).

This paper presents the results of studies on the development of compositions and technological parameters of light aggregate and light concrete based on the ashes slag of a FPC enterprise of Nova Zinc LLP (Karaganda region, Kazakhstan). Ashes slag is a loose wet mass of black color, which is removed after burning into the ashes slag dump by the method of hydraulic removal. The black color and the specific gloss of the ashes slag grains indicate the presence of a significant amount of unburned coal. The specific activity of natural radionuclides of AS is 33.0 Bq/kg, which is below the limit, in this regard, they can be used in housing construction without restrictions. The bulk density of ashes slag in its natural state is 632 kg/m³. The bulk density of ground and sieved through a sieve of 1.25 ashes slag is 440 kg/m³. The chemical compounds of ashes slag were determined by X-ray local spectral analysis (X-ray LA) using a JCTXA-733 electron probe microanalyzer. In (Table 1) shows the results of a chemical analysis of the initial AS.

The carbon content (C) is from 73.8 to 75.1%. According to the X-ray PA, the initial ashes slag in small amounts contains β - quartz (SiO_2) with lines d, Å: 4.26-3.35-2.45-2.28-2.12-1.672-1.542-1.454; mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) with lines d, Å: 5.41-3.83-3.35-2.70-2.52-2.28-2.20-2.12-1.840-1.523; anorthite ($\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) with lines d, Å: 4.06-3.83-3.21-3.13-2.52; hematite ($\alpha\text{-Fe}_2\text{O}_3$) with lines d, Å: 2.70-2.20 (Figure-1).

In (Table 2) shows the results of the chemical analysis of ash after burning at a temperature of 1000 °C.

After burning at 1000 °C in ashes slag, the residual fuel content is up to 43%. The peak intensities of quartz, mullite, anorthite, and hematite increased significantly. In addition, additional peaks of quartz d, Å: 1.814-1.607-1.378; of mullite d, Å: 2.84-2.01-1.607; of anorthite d, Å: 3.65-1.835-1.480-1.350 and hematite d, Å: 1.679 (Figure-1).

In (Figure-2) shows the result of differential thermal analysis (DTA) of the initial ashes slag. The thermal-analytical curve has endo- and exothermic effects. The endothermal effect at 120 °C is associated with the loss of physically bound water. The endothermal at 460 °C is associated with the softening of the glass phase.

Neoplasms in the thermogram are not observed. DTA showed that ashes slag weight loss is 70%. In (Table 3) shows the composition of the charges and the properties of the aggregate based on ash and loam after firing.

As can be seen from the table, lightweight aggregates obtained from mixtures No.4, 5, 6, and 7 in terms of bulk density and strength correspond to the requirements for lightweight aggregates. Figure 3 shows photographs of lightweight aggregates. As can be seen in the photographs, the aggregate samples from compound No.1 completely crumble. Granules of lightweight aggregates obtained from formulations No. 2 and 3 have a presentation. However, their surface crumbles, and they have low strength (easily crushed by fingers). This is due to the fact that in these compounds, the content of unburned coal is in the range of 42-56%, which burns intensively at a temperature of 900-1000 °C and significantly reduces the sintering ability of clay particles. Lightweight aggregate based on compound No.4 has satisfactory strength and can be used for the manufacture of lightweight concrete of low grades. The most optimal properties are lightweight aggregates obtained on the basis of compounds No. 5, 6, and 7.

Highly flexible bentonite clay has a high binding ability, but this alone did not give positive results. Aggregates containing 60-80% ashes slag also do not have the strength and easily crumble when squeezed by hand. Here the same effect of burning residual coal appears, which prevents clay sintering. However, samples with a content of 40-50% ash after firing at 1000 °C have a bulk density of 370-410 kg/m³ and a compressive strength in the cylinder of 1.2-1.7 MPa, which is two times higher than the strength of aggregates using loam.

For the manufacture of aggregate using clinker technology, almost all ashes and ashes slag mixtures obtained from the combustion of various types of coal can be used. For the preparation of mixtures, ashes slag were used 1-1.25 mm thick fractions. Using Portland cement as a binder, mixtures of 4 series were prepared. One series of compositions contained Portland cement and ashes slag; 2 series of compositions contained ashes slag, Portland cement and gypsum (mixed binder); 3 series of compositions contained ashes slag, Portland cement, and water glass; 4 series of compositions contained ashes slag, Portland cement and calcium chloride (CaCl₂). In the preparation of mixtures with Portland cement W/C, the ratio was 0.4-0.45. Water glass and CaCl₂ were introduced into the mixture with mixing water.

The addition of gypsum instead of part of the cement does not give positive results. With a mixed binder content of 25%, the aggregate has a bulk density of 514 kg/m³ and strength of 0.5 MPa, and after 14 days of hardening, its strength decreases to strength when the granules are easily crushed by fingers.

The addition of liquid glass (20-30%) together with water promotes rapid solidification; after 3 days of hardening under natural conditions, light aggregate granules acquired strength sufficient for its transportation and storage. The compressive strength in the cylinder after 14 days of hardening is 0.47-0.72 MPa. The addition of calcium chloride gives positive results. After hardening for 14 days in the air, the compressive strength in the filler cylinder is 1.2-1.3 MPa (Table 4).

Figure 4 shows samples of lightweight aggregates obtained by clinker technology based on Portland cement. The aggregate obtained on the basis of compound No.3 was used to calculate the composition of lightweight concrete according to the method described in the literature (Skramtaev, 1970).

The calculation showed that for the manufacture of 1m³ of light concrete, it is required: Portland cement - 385 kg; ashes slag aggregate - 265 kg; the rest: calcium chloride, quartz sand, and water. In order to replace quartz sand with ashes slag, the calculation of the flow rate of ashes slag by volumetric mass was performed. According to the calculation, the ashes slag flow rate was 290 kg instead of quartz sand.

Concrete samples were molded in the form of cubes measuring 100x100x100 mm on a laboratory vibrating table for 10-15 seconds. After molding, the samples were kept in metal form for 10-12 hours, then released from the molds. Further hardening of the products was carried out at room temperature for seven days, then the average density and strength of concrete were determined. Figure 5 shows the sample cubes of lightweight concrete obtained with quartz sand and with ashes slag sand.

After 21 days of hardening, the average density and strength of concrete were determined. The average density of concrete with quartz sand is 1700 kg/m³, and the average density of concrete with ashes slag sand is 1200 kg/m³. The compressive strength of concrete with quartz sand is 120 kg/cm², the strength of concrete with ashes slag sand is 80 kg/m². According to the values of compressive strength, they correspond to the brands M100 (B7.5) and M75 (B5), respectively. Determination of thermal conductivity showed that concrete on quartz sand has a thermal conductivity coefficient of 0.67 W/m·°C, concrete on ashes slag sand - 0.43 W/m·°C.

4. CONCLUSIONS

1. According to the requirements for ashes slag materials for the production of light aggregates and concrete, the residual fuel content should not exceed 10-17%. The ashes slag "Nova Zinc" LLP accepted for the study is characterized by a high content of residual fuel, which is up to 75%, i.e., 3-4 times higher than regulatory requirements.

2. For the first time, lightweight aggregates based on ashes slag with a high content of residual fuel were obtained. The optimal compounds of fired and non-fired lightweight aggregates are determined, as well as the technical parameters of their manufacture.

3. It has been found that for the manufacture of lightweight aggregate by firing, moderately

ductile loams, and highly ductile bentonite clay can be used. When using loam, the optimal content of ashes slag in the ceramic mass is 25-50%. When using bentonite clay, the content of ashes slag in the ceramic mass is 40-50%.

4. Using burning technology using loam, aggregates with a bulk density of 395-700 kg/m³, and compressive strength in the cylinder of 0.5-2.7 MPa were obtained. The light aggregates on bentonite clay after burning at 1000 °C have a bulk density of 370-410 kg/m³ and compressive strength in the cylinder of 1.2-1.7 MPa, which is two times higher than the strength of the aggregates using loam after burning at the same temperature.

5. With an increase in the content of ashes slag in the ceramic mass of more than 50%, as a result of intense burning of residual fuel in the temperature range 900-1100 °C, the sintering ability of clay particles decreases, which leads to a significant decrease in the strength of lightweight aggregate.

6. By clinker technology, using Portland cement as a binder, a aggregate with a bulk density of 595-600 kg/m³, and a compressive strength of 0.65-0.8 MPa in the cylinder was obtained. The addition of CaCl₂ as a cement hardening accelerator gives positive results. After three days of hardening in air, the strength of the light aggregate is 0.5-0.6 MPa, after 14 days - 1.2-1.3 MPa.

7. Using clinker aggregate and quartz sand, lightweight concrete samples were produced with a compressive strength of 120 kg/cm², an average density of 1700 kg/m³, and thermal conductivity of 0.67 W/m·°C. When replacing quartz sand with ashes slag sand, lightweight concrete was obtained with a compressive strength of 80 kg/cm², an average density of 1250 kg/m³, and thermal conductivity of 0.43 W/m·°C.

8. Indicators of the properties of light concrete samples in medium density and strength meet the requirements of GOST 25820-2014 "Light concrete". Technical conditions (TC) and their average density can be attributed to structural and structural-thermal insulation. Concrete strength class B7.5 and B5, respectively.

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Table 1. The chemical compound of the initial of ashes slag

SiO ₂	Al ₂ O ₃	TiO ₂	CaO	MgO	Fe ₂ O ₃	Na ₂ O	K ₂ O	SO ₃	Cl-ion
6.48	2.99	0.18	1.08	0.26	1.21	0.24	0.18	0.57	0.05

Table 2. The chemical compound of ashes slag, burned at 1000 °C

SiO ₂	Al ₂ O ₃	TiO ₂	CaO	MgO	Fe ₂ O ₃	Na ₂ O	K ₂ O	SO ₃	Cl-ion
24.27	11.34	0.53	3.77	1.01	3.97	0.71	0.66	1.3	-

Table 3. The compounds and properties of aggregates with loam

No.	Compound	1000 °C		1100 °C	
		Bulk density, kg/m ³	The compressive strength in the cylinder, MPa	Bulk density, kg/m ³	The compressive strength in the cylinder, MPa
1	Ashes slag (AS) – 80 % Loam – 20 %	impossible to determine	Granules crumble	impossible to determine	Granules crumble
2	AS – 70 % Loam – 30 %	325	Granules are easily crushed by fingers	314	Granules are easily crushed by fingers
3	AS – 60 % Loam – 40 %	415	Granules are crushed by fingers	400	Granules are crushed by fingers
4	AS – 50 % Loam – 50 %	441	0.55	395	0.5
5	AS – 40 % Loam – 60 %	511	0.9	495	0.8
6	AS – 30 % Loam – 70 %	658	1.6	670	1.5
7	AS – 25 % Loam – 75 %	700	2.7	687	2.4

Table 4. The optimal compounds and properties of aggregates with Portland cement

No.	Compound	ρ, bulk density	R, compressive strength in the cylinder, MPa	Hardening conditions
1	AS – 75 % Cement – 25 %	595	0.65	In a humid environment T= 22...25 °C. 14 days
2	AS – 70 % Cement – 30 %	600	0.80	In a humid environment T= 22...25 °C. 14 days
3	AS – 75 % Cement – 25 % CaCl ₂ – 3%	585	1.2	At room temperature, 14 days
4	AS – 70 % Cement – 30 % CaCl ₂ – 3%	590	1.5	At room temperature, 14 days

a

b

Figure 1. Diffraction patterns of the initial (a) and burned (b) ashes slag

Figure 2. The thermogram of the original ashes slag

Figure 3. Samples of aggregates after burning at a temperature of 1000 °C: a - compound No. 1, b - compound No.3, c - compound No. 4, d - No. 5, e – No.6, f – No.7. (see table 3)

a

b

a - Compound No. 2, b - Compound No. 3. (see table 3)