Modified heat-resistant concrete using slag aggregates

R A Burkhanova, T K Akchurin, I V Stefanenko
Department of Building Materials and Special Technologies, Volgograd State Technical University (VSTU), 1, Akademicheskaya St., Volgograd 400074, Russia
E-mail: renata_vlg@mail.ru

Abstract. The article investigates the sorption properties of modified heat-resistant concrete based on liquid glass and slag aggregates produced at Volzhsky Pipe Plant through the BET method. For the purpose of comparative analysis, the specific features of the changes in the sorption properties of heat-resistant Portland cement concrete and aluminous cement concrete as well as of ordinary concrete resulted from high-temperature heating have been determined. The adsorption isotherms of heat-resistant and ordinary concretes have been obtained. The data on the changes in concrete specific surface area due to an increase in the heating temperature and elongated duration of the exposure to high temperatures have been found. The authors have also revealed the changes in the structure and the properties of the materials under investigation depending on the type, composition and hygroscopic behavior of the components included.

1. Introduction

The scientific-technological progress in construction implies the use of a wide range of new efficient industrial structures and materials, a significant improvement of their quality and an enhancement of durability. In the fulfilment of this task, a considerable role is assigned to heat-resistant concrete and structures made of it. The use of large-size blocks and panels manufactured of such concrete and reinforced concrete allows developing new structural solutions, mechanizing the construction processes and eliminating handwork, reducing the costs and duration of construction, enhancing the performance reliability and service life of thermotechnical facilities. Thus, the task to enhance the crack resistance and durability of heat-resistant concretes is topical.

Based on the data of the sorption measurements over water vapours, the authors have conducted an investigation of the structure of concretes with further quantification of the specific surface area through the BET method [1,2]. The improved method of capillary condensation with regard to the volume of air entrainment pores allows obtaining complete information on the volume of the pore space in a material and making it considerably more precise within the range of the pore sizes smaller than 10-7 m.

2. Method of an investigation of the structure of concretes with further quantification of the specific surface area through the BET method

In the course of the work, the authors determined the sorption properties of modified heat-resistant concrete based on liquid glass and slag aggregates with fine-ground slag additive produced by Volzhsky Pipe Plant (VPP OJSC). For the purpose of comparison, heat-resistant concretes on Portland cement and aluminous cement as well as ordinary concrete were studied [3,4]. The specific features of
the changes in the sorption properties of the specified types of concrete resulted from high-temperature heating were detected [5].

The slag crushed stone from electric-furnace steelmaking at Volzhsky Pipe Plant is a loose material of dark-grey metalexcent color, characterized by the fineness of 10 - 20 mm, the void ratio of 0.43; the poured bulk density of 1.380 – 1.400 g/sm³; the true density of 2.3 g/sm³. Its chemical composition is presented in table 1:

| Title of material       | CaO   | SiO₂  | Al₂O₃ | Fe₂O₃ | MgO  |
|-------------------------|-------|-------|-------|-------|------|
| Smelter slag (coarse)   | 24.6  | 18.8  | 12.3  | 22.3  | 11.4 |
| Smelter slag (fines)    | 21.3  | 20.7  | 14.6  | 25.5  | 13.3 |
| Smelter slag (fractions 0-10) | 19.1 | 25.8  | 4.8   | 13.9  | 13.9 |

The given material has the following quality profile:
- the grade according to the ultimate compressive strength – M 1200;
- the grade according to abrasion resistance - I 1;
- the poured bulk density - 1530 kg/m³;
- the value of the specific effective activity of naturally occurring radionuclides – to 370 Bq/kg;
- the frost resistance of no less than the grade - F50;
- the content of dust and clay particles - no more than 0.6%.

The macrostructure of the slag is porous; it contains a crystallized glass-like component the particles of which have the colour ranging from colourless to reddish brown. The latter is indicative of the presence of ferrous oxides in the structure. The X-ray crystal structure analysis (figure 1) confirms that the smelter slag formed as a result of slow cooling has completely crystallized and contains almost no glass [6-8].

The fact that the fine-ground slag is characterized by practically zero ability to harden at ordinary temperature without activating additives is explained by a low content of active phases in it. Therefore, for the purpose of the given investigation, fine-ground slag from VPP was used as a micro-aggregate for fine grain concretes [9].

The concrete accepted for the investigation was first heated to the temperatures of 105, 300 and 800°C. The rate of the temperature elevation was preset as 100°C per hour, the exposure time at the designed temperature was 72 hours, the rate of cooling was 40°C per hour. Two series of weighting of 30 - 50 g. were used. One of the series was intended to obtain the adsorption data, while the other – the desorption data. The point on the desorption curves (P/Pₘ = 0.98) was determined after the preliminary vacuum-saturation of the concrete with water (1.10 - 4 mmHg) [10,11].

The drying process of the samples aimed at obtaining the initial point on the adsorption curve for the concrete which was not exposed to heating as well as the determination of the equilibrium moisture content (the amount of the evaporated moister) at all the accepted values (P/Pₘ) were carried out through the «D»-method (figure 2) owing to the difference of the pressures and temperatures in the exsiccator and the ambient environment. The cooling of the moisture collector trap was conducted
above carbon dioxide ice at the temperature of \(-79^\circ C\) (the pressure of the water vapours in the exsiccator over the samples was 5.10 mmHg).

\[
d \times 10^{-10}, \text{ m}
\]

**Figure 1.** The X-ray pattern of smelter slag. \(d\) – the distance between the planes, m; \(\theta\) – the angle between the direction of the beam and the planes reflecting the rays, degree

\[
\begin{array}{cccccccc}
4.0 & 14.0 & 24.0 & 34.0 & 44.0 & 54.0 & 64.0 \\
10.78 & 4.322 & 3.786 & 2.423 & 2.000 & 1.566 & 1.248 \\
4.715 & 3.306 & 2.462 & 2.132 & 1.873 & 1.590 & 1.348 \\
\end{array}
\]

**Figure 2.** The scheme of the drying installation for samples: 1 – to the pump; 2 – carbon dioxide ice with alcohol; 3 – insulation; 4 – exsiccator; 5 – samples; 6 – air inlet.

The sorption isotherms of water vapours were obtained through the equilibrium moisture content of concrete above saturated salt solutions (figures 3-7). The temperature in the chambers was kept constant (20°C), the humidity was controlled with humidity sensors and simultaneously according to the temperature applying dry-bulb and wet-bulb thermometers.

According to the results of the investigation, the sorption characteristics of heat-resistant concretes with liquid glass and slag aggregates based on Portland-cement or aluminous cement as well as of ordinary concrete differ depending on the type, composition and hygroscopic properties of the
components included. Hysteresis is typical for the adsorption isotherms of heat-resistant and ordinary concretes as well as of porous aggregates [12-14].

Figure 3. I - isotherm of desorption of heat-resistant Portland-cement concrete which was not exposed to heating; II - isotherms of adsorption and desorption after the heating at the temperature of 105°C; III - isotherms of adsorption and desorption after the heating at the temperature of 300°C; IV - isotherms of adsorption and desorption after the heating at the temperature of 800°C.

Figure 4. The influence of heating on the change in the sorption properties of heat-resistant Portland-cement concrete. I - adsorption: 1, 2, 3 after the heating at the temperatures of 105, 300, 800°C; II - desorption: 1 - the concrete was not exposed to heating, 2, 3, 4 - after the heating at the temperatures of 105, 300, 800°C.
Figure 5. Isotherms of sorption of water vapours by heat-resistant aluminous cement concrete: 1 – the concrete was not exposed to heating; 2,3,4 – after the heating at the temperatures of 105, 300, 800°C, respectively.

Figure 6. Isotherms of desorption of water vapours by heat-resistant liquid glass concrete: 1 – the concrete was not exposed to heating; 2,3,4 – after the heating at the temperatures of 105, 300, 800°C, respectively.

Figure 7. Isotherms of desorption: 1 - expanded-clay concrete; 2,3 – ordinary concrete with carbonate and granite aggregates, respectively.

The specific surface area of concrete was obtained through the data of the sorption measurements applying the BET method [1], the basic equation to calculate the specific surface area (S) of capillary porous materials has the following form [3, 15-17]:

\[ S = \frac{a_m N}{M} \times A_m \]  

where \( a_m \) – is the capacity of the monomolecular layer; \( M \) – is the molecular mass of the adsorbate; \( A_m \) – is the area occupied by a molecule of adsorbate within the filled monolayer; \( N \) – is Avogadro's number.

The value of \( a_m \) was determined from the linear form of the BET equation [2]:

\[ \frac{P / P_s}{a(1 - P / P_s)} = \frac{1}{a_m c} + \frac{C - 1}{a_m c} \cdot P / P_s \]  

where: \( a \) – is the adsorption at the corresponding relative pressure \( P/P_s \) per unit mass of the adsorbent (concrete); \( C \) – is the constant related to the heat of absorption and the temperature. The value of \( C \) was used for approximate calculation of the heat of adsorption:
\[ Q_l - L = RT \ln C \]  
(3)

where: \( R \) – is the gas constant; \( T \) – is the absolute temperature; \( Q_l \) - is the heat of adsorption in the first layer and \( L = 44 \times 10^6 \) J/kmol – is the latent heat of condensation at the temperature of 20°C.

The substitution of the experimental data at \( P/P_s < 0.45 \) into the equation (2) allows determining the slope angle (\( \phi \)) of the straight line \( (C - I) / a m \) intercepting a segment \( a = I/ am C \) on the ordinate axis.

The value of \( \tan \phi = b = (C - I) / (amC) \).

The values of \( a_m \) and \( C \) were determined from the equations:

\[ a_m = \frac{1}{a + b} \quad \text{and} \quad C = \frac{b}{a} + 1. \]  
(4)

The investigations showed that the heating of concrete leads to a reduction in their sorption moisture content, especially at the temperature of 800°C [18-21]. This allows quantifying the structural changes occurring in concrete as a result of the heating. Depending on the type and composition of heat-resistant concretes, their specific surface area before heating amounts to 40-80 m²/g and it significantly decreases under heating. The influence of heating on the change in the structural characteristics of heat-resistant concretes is presented in tables 2, 3.

### Table 2. Structural characteristics of heat-resistant modified concrete using slag aggregates (MCS) and heat-resistant Portland-cement concrete (HPC)*.

| Temperature of concrete heating, °C | Specific surface area S, m²/g | Heat adsorption of C, J/kmol | \((Q_l - L) \times 10^6\), J/kmol | Porosity W, % |
|-----------------------------------|--------------------------------|-------------------------------|---------------------------------|--------------|
| 20                                | 44.8                           | 13.4                          | 6.14                            | 36.40        |
|                                   | 40.0                           | 22.64                         | 7.50                            | 27.4         |
| 105                               | 42.20                          | 16.13                         | 6.78                            | 33.00        |
|                                   | 40.00                          | 20.41                         | 7.23                            | 26.3         |
| 300                               | 41.00                          | 7.82                          | 4.68                            | 33.7         |
|                                   | 40.70                          | 9.14                          | 5.11                            | 26.0         |
| 800                               | 23.7                           | 13.32                         | 6.12                            | 42.2         |
|                                   | 24.7                           | 14.25                         | 6.30                            | 33.1         |

* MCS is over the line, HPC is under the line.

### Table 3. Structural characteristics of heat-resistant aluminous cement concrete (HAC) and ordinary concrete based on Portland-cement (OC)*.

| Temperature of concrete heating, °C | Specific surface area S, m²/g | Heat adsorption of C, J/kmol | \((Q_l - L) \times 10^6\), J/kmol | Porosity W, % |
|-----------------------------------|--------------------------------|-------------------------------|---------------------------------|--------------|
| 20                                | 77.88                          | 49.21                         | 9.44                            | 26.8         |
|                                   | 28.67                          | 8.2                           | 4.8                             | 16.2         |
| 105                               | 22.65                          | 20.74                         | 7.27                            | 26.1         |
|                                   | 21.59                          | 17.05                         | 6.75                            | 15.6         |
| 300                               | 26.19                          | 89.28                         | 10.93                           | 28.6         |
|                                   | 10.11                          | 28.43                         | 8.07                            | 14.7         |
| 800                               | 24.78                          | 140.48                        | 12.05                           | 28.5         |

* HAC is over the line, OC is under the line.
3. Conclusion and findings
As a result of the investigation, it was revealed that heating of concretes leads to a reduction in their specific surface area. In addition, this reduction in ordinary concrete (OC) is of smoother nature than in heat-resistant aluminous cement concrete (HAC), especially when the values of the specific surface area (S) at normal temperature and after the heating at the temperature of 105°C are compared. The change in the value of S in the heat-resistant Portland-cement concrete (HPC) differs from that in the heat-resistant aluminous cement concrete (HAC). An insignificant change in the specific surface area within the temperature range of 20-300°C followed by an abrupt reduction in the value of S after the heating at 800°C is typical of HPC. Under the equal conditions, the behaviour of the specific surface area of lightweight modified heat-resistant concrete (MCS) under heating is closer to that of OC and HPC than to that of HAC. The absolute values of S of HAC turned out to be the largest at the normal temperature, while the values of S of HPC and MCS are close under heating within the temperature range of 20 to 800°C.

The reduction in the specific surface area of concretes occurs not only with a rise in the heating temperature, but also with an increase in the duration of the exposure to high temperatures. The higher the temperature and the longer the exposure to heating are, the greater the degree of the reduction in the specific surface area of concrete is.

Heating of concretes applying high temperatures leads to significant changes in their structure. The total volume of pores changes, a redistribution of the pore volumes according to their structures takes place, which in its turn results in the changes in the ratio of the quantities of fine and coarser pores.

The data concerning the changes in the pore structure of heat-resistant and ordinary concretes under heating have been obtained. Heating of heat-resistant Portland-cement concrete causes the coarsening of its pore structure; a redistribution of the pore volumes according to their sizes takes place. With inconsiderable changes in the total porosity, the average radius of concrete pores increases due to the reduction in the volumes of fine pores. Heat-resistant aluminous cement concrete differs from the other types of heat-resistant concrete by its coarse pore structure. In the unheated concrete as well as in that heated at the temperatures of 105, 300 and 800°C the volume of the pores with the radius of less than 10^-7m ranges from 25% to 36% of the total pore volume which equals to 26-29% of the total volume of the material. Larger pores occupy the rest of the volume, which approximately corresponds to the pore distribution in chamotte. When compared to the abovementioned type of concrete, ordinary concrete has a fine pore structure. Thus, within the temperature range of 20 to 600°C, the total porosity of ordinary concrete is the lowest and, with regard to air entrainment pores, it changes within the limits from 16% to 19% depending on the temperature of concrete heating. At the same time, the volume of the pores with the radius of less than 10^-7m amounts up to 72% of the total volume. Both ordinary concrete and heat-resistant Portland-cement concrete belong to the materials with fine pore structure. Therefore, in the course of drying and the first heating to operating temperatures, the structure of Portland-cement concrete shows higher hydrodynamic resistance to the movement of moisture in the form of liquid or vapour and considerably lower permeability to gas than the structure of aluminous cement concrete.

The sorption properties of heat-resistant concretes depend on the type, composition and the hygroscopic properties of their components. Along with this, the finer the pores in the material are, the sooner capillary condensation starts.

References
[1] Brunauer S 1946 The adsorption of gases and vapors (Moscow: Foreign Languages Publ House) p 781
[2] Gregg S J, Sing K S W 1970 Adsorption, surface area and porosity (Moscow: Mir Publishers) p 407
[3] Fedyanina A V, Akchurin T K, Grigoryevsky V V 2013 Influence of heating on the changes in capillary porous structure of lightweight concrete with expanded-clay aggregates through the sorption BET method Engineering Issues of Materials Science in Construction, of
Geothechnical and Road-building Construction Proceedings of the IV International Scientific-Technical Conference, VSUACE pp 241–245

[4] Mohammeda M K, Al-Hadithi A I, Mohammed M H 2019 Production and optimization of eco-efficient self compacting concrete SCC with limestone and PET Construction and Building Materials 197 734–746

[5] Shevchenko V I, Cherednichenko T F, Grigoryevsky V V 1991 Developing the theory and methods to determine the characteristics of crack resistance and durability of concrete VolgCEI, report on SRW 2.1–91 72–73

[6] Gadzhiev A M, Kurbano R M, Khadzhihalaykov G N, Hezhev T A 2017 The influence of the filler grain composition on the properties of the heat-resistant basaltic concrete Herald of Dagestan State Technical University. Technical Sciences 44(3) 146–155

[7] Bazhenov Yu M, Alimov L A, Voronin Yu V 1997 Forecasting the properties of concrete mixtures and concrete with technogenic wastes News of higher educational institutions. Construction 4 68–72

[8] Danilovich I Yu, Skanavi N A 1988 Use of furnace clinkers and ashes for construction materials manufacturing (Moscow: Vysshaya Shkola Publ) p 72

[9] Balakrishna M N, Mohamad F, Evans R, Rahman M M 2020 Durability of concrete with differential concrete mix design International Research Journal of Engineering and Technology (IRJET) 7 (4) 696–701

[10] Volkov Yu S 1994 Use of extra-high-strength concrete in construction Beton and Zhelezobeton (Concrete and Reinforced Concrete) 7 27–31

[11] Batrakov V G 2002 Modified concretes in modern construction practice Industrial and Civil Engineering 9 23–25

[12] Vysotsky S A 1990 Optimisation of the composition of concrete with disperse mineral additives Beton and Zhelezobeton (Concrete and Reinforced Concrete) 2 7–9

[13] Dvorkin L I, Dvorkin O L 2007 Construction materials manufactured of industrial wastes (Rostov-on-Don: Phoenix) p 368

[14] Krasnov A M 2003 Highly filled fine-grained concrete of enhanced strength Stroiteln’ye Materialy 1 8–10

[15] Latysheva L Yu, Smirnov S V 2000 New-generation concrete for fast and strong construction Construction Materials, Equipment, Technologies of the XXI Century 3 17–19

[16] Protalinsky A N 2003 Modifying of concrete structure with wastes from Western Siberia industry Problems and methods of creation of composite materials and technologies of integrated metal recovery from secondary mineral resources: collected papers of scientific-practical seminar pp 188–197

[17] Rakhimov R Z 2002 Development and implementation of software package "CONCRETE" for design and correction of high-performance concretes Beton and Zhelezobeton (Concrete and Reinforced Concrete) 6 2–5

[18] Al-Hadithi A I, Hilal N N 2016 The possibility of enhancing some properties of self-compacting concrete by adding waste plastic fibers Journal of Building Engineering 8 20–28

[19] Dvorkin L I 1991 Cement concrete with mineral aggregates (Kyiv: Bud'vel'nik) p 133

[20] Saenko S M, Ochkina N A 2001 Specialized fine-grained concretes of enhanced density Abstracts of the 6th Intern. Seminar "Construction and finishing materials. Standards of the 21st century" pp 61–62

[21] Kharkhardt A N 1996 A way of obtaining high-density compositions of granular raw materials News of higher educational institutions. Construction 10 56–60