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PRODUCTION OF POROUS GEOPOLYMERS USING ASH AND SLAG WASTE OF POWER PLANTS IN THE RUSSIAN ARCTIC

Coal combustion at thermal power plants generates much ash and slag waste which amass at waste sites and have a dramatic adverse effect on the environment. In the meanwhile, ash and slag is a valuable source for the production of silicate materials for road making and civil construction. The most promising technology for the synthesis of silicate materials is selected from the viewpoint of energy and resource efficiency–the low-temperature alkaline activation and production of porous geopolymers. A range of mix formulations is developed on the basis of ash and slag from Severodvinsk PP-1, with addition of an alkaline activator (mixture of sodium hydroxide solution and liquid glass), various sponging agents and a foam stabilizer. The increase in the amount of an alkaline activator noticeably decreases the foam stability. The aluminum powder is a less active sponging agent as compared with the hydrogen peroxide solution. The introduction of a foam stabilizer essentially increases the number of pores and decreases the foam density. The synthesis of geopolymeric materials using ash and slag from Apatity PP produced a material with the density of 456 kg/m^3 and with the pores 300–600 μm in size upon average. Addition of a surfactant greatly decreases the average size of pores at insignificant reduction in the density of the test samples. On the evidence of the research, the optimal composition of the activation mixture is selected for manufacturing porous geopolymeric materials with a density less than 500 kg/m^3, including an alkaline activator, hydrogen peroxide as a sponging agent and a surfactant as a foam stabilizer.

Keywords: *ash and slag waste, thermal power plants, recycling, geopolymers, porous structure, road construction, Arctic zone*
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Introduction

Coal-fired generation makes around 40% of electric power and up to 60% of thermal power. In the Arctic zone of Russia, for example, coal-fired generation is quite substantial (20% upon average). Almost each Arctic region holds at least one large-yield backbone coal-fired power plant. Coal combustion generates much waste (to 15% of coal mass) in the form of ash and slag (AS) waste [1, 2]. By 2020 Russia accumulated 1.8 Bt of AS, and the volume grows annually by 20–25 Mt. The AS waste sites cause air and water pollution and damage landscapes, which has an essential adverse impact on the environment in adjacent areas. The composition of AS mainly includes oxides of silicon, aluminum, iron, alkali and alkali-earth metals, which makes this kind of waste a valuable source of minerals for production of silicate materials for the road and civil construction [3–11].

The road construction under conditions of permafrost and extreme climate in the Arctic zone of Russia is a challenging problem. The major difficulties in the road construction and usage in the Arctic arise from the unpredictable behavior of permafrost. Capillary saturation of clay-bearing soil with water runs unevenly. Freezing of such soil causes nonuniform increase in its volume; this process is called heaving which bitterly deforms roadbeds. Prevention of frost heave includes construction of extra anti-frost heavy courses using various antibonding materials, for example, crushed rock, sand or expanded-clay pebble [12, 13].

The most effective and endurable materials for making anti-frost road pavement is granulated foam glass and other porous silicate fillers. In view of resource and energy efficiency, it is most promising currently to use porous geopolymers. Geopolymers form in interaction between aluminum silicate and an alkali component. The resultant colloidal suspension passes the stages of polycondensation and solidification without thermal treatment, and possesses all properties of traditional silicate materials [14, 15]. This technology is advantageous for avoiding high-temperature treatment and providing structurization under temperatures below 100 °C. The wide range of applicable aluminum silicates includes both natural (metakaolinite, sand, clay) and manmade (glass, bauxite slurry, power generation ash and slag) products, and their combinations [15, 16]. Accordingly, production of geopolymers from industrial waste can solve a number of critical problems, including waste recycling, reduction in the environmental pressure and enhancement of economic efficiency owing to waste usage and application of low-temperature technologies. Eventually, this study aimed to develop a technology for integrated recycling of power plant ash and slag in manufacture of porous geopolymers for the needs of road construction in the Arctic zone of Russia.

Research procedure

The manufacture of geopolymer foams for the tests included: ash and slag from Apatity and Severodvinsk Power Plants; activator solution of liquid glass (44.5% (mass) water solution of sodium silicate, silica ratio SiO_2:Na_2O = 2) and NaOH (12 M water solution); sponging agent (aluminum powder or 30% hydrogen peroxide solution); surfactant or foam stabilizer (sodium stearate) [14–17].

Applicability of the test waste was confirmed based on the waste chemistry (**Table 1**) and phase composition (**Fig. 1**). The chemical composition of ash and slag was analyzed at an accredited laboratory at the Institute of Geology of Ore Deposits, Petrography, Mineralogy and Geochemistry, RAS, Moscow, on the X-ray fluorescence spectrometer PW2400 (Philips Analytical). The phase composition was determined on Thermo Fisher Scientific ARL X'TRA X-ray powder diffraction instrument at the Shared Use Center Nanotechnologies of the Platov South-Russian State Polytechnic University.

The results exhibit similarity of the two test types of AS. The dominant oxides in both cases are SiO_2, Al_2O_3 and Fe_2O_3. The oxides of alkali (sodium, potassium) and alkali-earth (calcium, magnesium) metals are present in amount of a few percent. The phase composition shows that the waste is a glass crystalline material. The low intensity of the crystal peaks and the present of the so-called amorphous halo in the range of 20–30° is reflective

Table 1. Ash and slag chemistry

AS source	Chemical composition*, % (mass)										
	Na_2O	K_2O	MgO	CaO	Fe_2O_3	Al_2O_3	SiO_2	TiO_2	P_2O_5	SO_3	ППП
Apatity PP	0.78	1.94	2.63	3.59	7.73	22.15	52.39	1.05	0.36	0.37	6.05
Severodvinsk PP-1	3.54	2.29	2.71	2.07	5.93	17.67	60.75	0.82	0.21	0.32	2.29
*Oxides at the content higher than 0.1% (mass)											

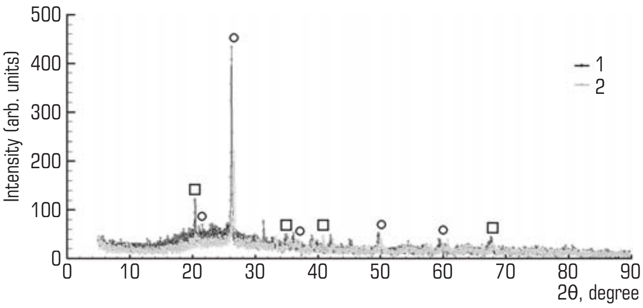

Fig. 1. Ash and slag phase composition:

1–AS from Severodvinsk PP-1; 2–AS from Apatity PP; ○–quartz/tridymite (SiO_2); □–anorthite ($CaAl_2Si_2O_8$)

of appreciable amorphous glass phase. The crystalline phase represents a mixture of quartz and tridymite (polymorphous modifications of SiO_2), as well as embryo anorthite $CaAl_2Si_2O_8$. Thus, the test ash and slag from Apatity PP and Severodvinsk PP-1 is the aluminum silicate material with the high content of the amorphous phase, which is an indication of this waste exploitability as a source material for the synthesis of geopolymers.

Manufacture of geopolymeric mixtures was stage-wise. The ash and slag waste was first dried at 105 ± 5 °C for 4 hours and milled down to a size less than 250 μm. The alkaline activating agent was prepared in a separate bulb by mixing powder NaOH and water up to a preset concentration of the solution added then with liquid glass. The mix was stirred for 10 min and then added to the AS powder and stirred for 10 min again. The resultant blend was added with a sponging agent, represented by powdered aluminum Al with particles less than 100 μm or 30% hydrogen peroxide solution H_2O_2, and with foam stabilizer—surfactant sodium stearate (if necessary), and was stirred for 5 min. After that, the mixture was poured in cylindrical cells with a diameter of 23 mm and 25 mm high. The samples were held at the room temperature for 7 days to maintain polymerization, polycondensation and solidification.

The average density ρ (kg/m^3) is found from the formula:

$\rho = 1000m/(\pi r^2 h)$,

where m is the weight of a sample, g; r is the radius of a sample, cm; h is the height of a sample, cm.

Each entry of a test value is the average of 5 measurements.

The microstructure of the cross-sections of the porous geopolymeric samples was analyzed on optical microscope Bresser Duolux 20x-1280x.

Experimentation

First, the optimal amount of the alkaline activator (AA) for manufacturing porous geopolymers was determined. The resultant blend compositions are described in **Table 2**. The mixtures were added to 100% (mass) AS [16]. For the stability analysis of the foam, the sodium stearate powder was added in amount of 1% (mass) over 100. The series A samples include aluminum powder as a sponging agent, the series H—hydrogen peroxide H_2O_2, the samples with a surfactant have an index s. **Figures 2** and **3** describe the internal structure of the samples and their density change, respectively.

The results distinctly evince mechanisms of formation of a porous structure during geopolymerization with different modifiers. For example, with an increasing amount of the alkaline activator, the foam markedly loses stability. For instance, with addition of 35% (mass) AA, macropores larger than 500 μm occupy the whole volume of the sample. When AA amount is increased to 60% (mass), the pore formation intensity drops, which ends with the two times higher density of a sample. Addition of 85% (mass) AA annuls pore formation, and the density of the samples exceeds 1500 kg/m^3.

The aluminum powder is a less active sponging agent than H_2O_2. The hydrogen peroxide solution generated coarse (0.5–2 mm) open and intercommunicating pores in compositions 1 and 2. Addition of a surfactant produced

Table 2. Compositions of geopolymeric blends with different contents of alkaline activator

Composition no.	Content, % (mass)		
	AS	Alkaline activator	Sponging agent (Al or H_2O_2)
1	100	35	3
2	100	60	3
3	100	85	3

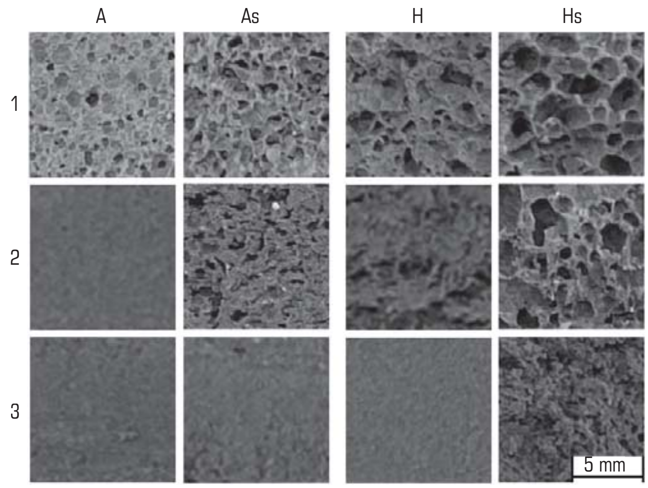

Fig. 2. Internal structure of synthesized samples: 1—composition 1; 2—composition 2; 3—composition 3; A—sponging agent Al_2O_3; H—sponging agent H_2O_2, s—surfactant added

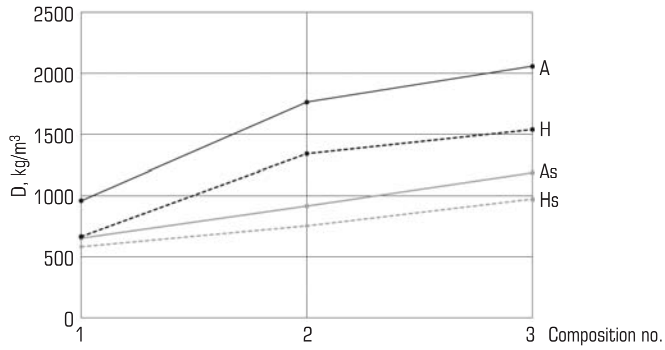

Fig. 3. Density of geopolymer samples versus its composition: 1—composition 1; 2—composition 2; 3—composition 3; A—sponging agent Al_2O_3; H—sponging agent H_2O_2, s—surfactant added

a porous material with the density of 974 kg/m^3 in case of composition 3 as well. Foam formation with the aluminum powder was only observed in composition 1: the pores were 0.4–1.0 mm in size, and the density was 961 kg/m^3. Introduction of a surfactant ensured porous structure in composition 2 with the density of 916 kg/m^3, while composition 3 lacked foam totally.

In this manner, a surfactant (foam stabilizer) represented by sodium stearate essentially improves the process of pore formation. After addition of the surfactant, the number of pores noticeably grows, and the generated foam has a density less than 1200 kg/m^3 even in compositions with 85% (mass) AA. Depending on the initial composition, stabilization of foam can take place either across the whole volume of a sample, or only at the top of it while the bottom settles out into a dense material (**Fig. 4**).

On the strength of the obtained results, geopolymeric materials were synthesized using AS from Apatity Pp. The basic composition was 1H (35%

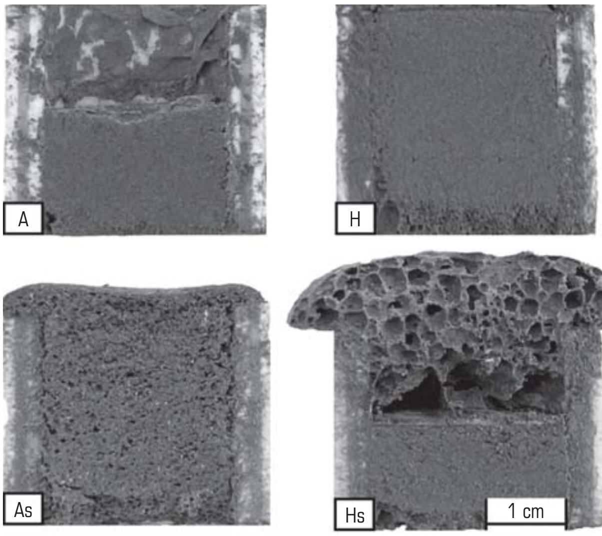

Fig. 4. Foam stabilization with surfactants: A—sponging agent Al_2O_3; H—sponging agent H_2O_2, s—surfactant added

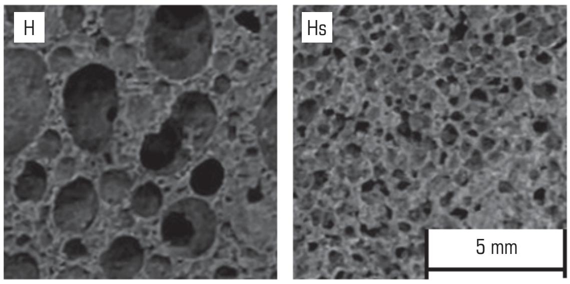

Fig. 5. Internal structure of porous geopolymers made of ash and slag from Apatity PP: H—sponging agent H_2O_2, s—surfactant added

(mass) AA, sponging agent H_2O_2) with and without addition of a surfactant. **Figure 5** demonstrates the internal structure of the manufactured samples.

The test results reveal another important function of the surfactants, namely, prevention of coalescence of pores. In Fig. 5 the average diameter of the pores in the sample free from the surfactant is 800–2700 μm, while with addition of the surfactant, the pores diminish in size down to 300–600 μm. On the other hand, the density of the samples decreases not very much and makes up 571 kg/m^3 and 456 kg/m^3 in the compositions without and with the surfactant, respectively. This fact confirms the relevance of the studies into physical and mechanical properties of porous materials, and into porous structure parameters.

In such a way, on the evidence of the accomplished research, the optimal composition for manufacturing a highly porous geopolymeric material is composition 1Hs containing 100% (mass) AS, 35% (mass) AA, 3% (mass) sponging agent H_2O_2 and 1% (mass) sodium stearate surfactant. Subject to the type of ash and slag, the specified composition allows manufacturing materials with a density less than 600 kg/m^3 and with uniformly distributed pores 300–700 μm in size.

Conclusions

Synthesis of constructional materials from manmade waste is a relevant trend of research. Manufacture of porous geopolymers using ash and slag of domestic power plants enables production of efficient and endurable materials, and ensures reduction in the environmental pressure owing to recycling and depletion of accumulated ash and slag waste. The accomplished research has demonstrated manufacturability of porous geopolymers using ash and slag from different power plants in the Arctic zone, and described the influence of the components of a blend on the structure formation processes. The optimal amount of an alkaline activator and the most efficient sponging agent are selected, and the expediency of adding a surface active substance to act as a foam stabilizer toward formation of a uniform finely porous structure is substantiated. The obtained results are usable in production of porous geopolymers from ash and slag waste.

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