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Obtaining a Geopolymer Hybrid Binder Based on Thermal Energy and Metallurgy By-Products

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Nowadays, one of the significant issues for the construction industry is the shortage of materials due to the increased volume of work, as well as their rising cost due to the recently imposed anti-Russian restrictions. The most dynamically increasing in price and the most required material in construction at the moment is Portland cement binder. Portland cement production is responsible for more than 7% of the world's carbon dioxide emissions and is a constant source of environmental concern in the neighbouring areas. The solution to these issues could be the creation of a geopolymer binder of hybrid composition from secondary materials of the metallurgical and heat and power industries by their alkaline activation. The purpose of the study was to assess the degree of influence of each mixture component, its content and curing conditions on the mechanical properties of the resulting binder. The results of the study show the possibility of obtaining the required strength values without heat and humidity treatment during the gaining of strength, which allows the hybrid binder to be regarded as an analogue of Portland cement.

Key words: construction, roads, binder, geopolymers, fly ash, blast furnace slag, Portland cement

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НАУЧНАЯ СТАТЬЯ
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Получение геополимерного вяжущего гибридного состава на основе побочных продуктов теплоэнергетики и металлургии

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Значительными проблемами строительной отрасли, при общем увеличении объема производимых работ, являются дефицит и удорожание материалов в связи с введенными антироссийскими санкциями. В настоящее время динамично растущим в цене и необходимым в строительстве материалом является портландцементное вяжущее. Производство портландцемента отвечает более чем 7% эмиссии углекислого газа в мире и вызывает опасения по поводу экологической обстановки на окружающих территориях. Решением указанных проблем может стать создание геополимерного вяжущего гибридного состава с включением вторичных материалов металлургической и теплоэнергетической промышленности, подвергнутых щелочной активации. Проведено исследование с целью оценки степени влияния компонентов смеси, их содержания и условий твердения на механические свойства вяжущего. Показана возможность достижения требуемой прочности строительного материала без тепловлажностной обработки, что позволяет рассматривать гибридное вяжущее как аналог портландцемента.

Ключевые слова: строительство, автомобильные дороги, вяжущее, геополимеры, зола-унос, доменный шлак, портландцемент

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INTRODUCTION

The volume of road construction in the Russian Federation has increased significantly due to the national project "Safe Quality Roads". Natural increase in the volume of construction work causes a shortage of inert materials and promotes the involvement of local materials in the construction process. Furthermore, the imposing of anti-Russian restrictions has had a significant impact on the cost of Portland cement binders [1]. In order to solve these issues and create the inorganic hybrid binders, it was proposed to use secondary materials from the thermal power and metallurgical industries, of which 1.6 [2] and 5.4 [3] billion tonnes, respectively, have been accumulated in the Russian Federation.

Hybrid binders are artificially synthesised inorganic materials with a polymer structure repeating the atoms of silicon and aluminium in their chains [4]. Depending on the interchanging of the silicon and aluminium atoms, they are subdivided into:

– poly(sialat) (- Si – O – Al – O -);
– poly(sialat-siloxo) (- Si – O – Al – O – Si – O -);
– poly(sialat-disiloxo) (- Si – O – Al – O – Si – O – Si – O -) [5].

The systematic research on geopolymer binders (cements) is relatively recent. They began with Joseph Davidovits's [5] research in the 1980s while analysing samples of ancient Egyptian structures from artificially built rocks [6]. Davidovits established the basic theses of a new theory about geopolymer binders, which are being actively used in the archaeological study, in the search for ways to dispose toxic waste and create geopolymer concretes from natural rock. There is no doubt that Davidovits, who has been active for more than 40 years at the Institute of Geopolymers in France in the study of geopolymer concretes, is the world's best known and the most competent specialist in the field of geopolymer cements. However, his research is largely linked to that of archaeological monuments, which contain no waste from the energy and metallurgical industries and differ considerably from natural materials. Also he did not consider the use of granulated slags which have a different mineral composition compared to slow-cooling blast furnace slags. In addition, all the studies were based on fly ash which is prevalent in Europe but not available in sufficient amounts in Russia.

Many researchers worldwide are studying binders produced by alkaline activation of alumino-silicate raw materials. The leading experts mainly focus on studying geopolymers based on fly ash [7], zeolite [8], metakaolin [9] and other clay materials [10, 11]. There are several studies on the activation of waste marble, travetin and volcanic tuff [12]. Meanwhile features of creating geopolymer binders on the basis of ash-and-slag mixtures are practically not studied all over the world (due to hydration at the dump their chemical composition differs from fly ash composition, and due to ash removal technology the particle size, shape etc. also cause differences of fly ash from ash-and-slag mixture). In addition, the composition of fly ash of different genesis has not been investigated.

The most common hybrid binders consist of fly ash with the addition of ground granulated blast furnace slag [13], providing increased strength and water absorption resistance of the geopolymer due to its lower sorption capacity. If the slag content of the hybrid binder is low, the high strength properties of the binder can be achieved by steaming at 600C[14]. The activators of these binders are silicates [15] and sodium hydroxide [16], potassium hydroxide, phosphoric acid [17], etc. Sodium hydroxide increases the reaction speed and dissolves the solid alumino-silicate, while the potassium hydroxide improves the degree of polymerisation [18]. The disadvantage of alkaline binder activation is the presence of free sodium hydroxide, which causes alkaline corrosion of metals [19]. The paper

[20] mentions that corrosion can be caused by high concentrations of carbon dioxide, so the use of hybrid binders in combination with reinforcement is undesirable. Phosphoric acid additives cause a reduction in the strength of the geopolymer after soaking, which has a negative effect on the quality of structures used outdoors [17].

The properties of the future binder are influenced by: the Si/Al ratio of the raw material; the type and amount of the alkaline activator; the temperature and curing conditions; the introduction of additional additives if a porous binder similar to foamed concrete [18] is desired. The purpose [21] of the study was to investigate the effect of the Si/Al ratio on the properties of future hybrid binders. It is possible to adjust this ratio by adding materials containing high amounts of silica to the mixture; an example of such a material is ash from rice hulls. The results show that this ratio has a negligible effect on the characteristics.

The strength of this type of inorganic binder can reach values between 40 and 80 MPa, while binders with a strength of 25 MPa [22] or more are suitable for construction purposes.

The purpose of our study is to find an optimal mix ratio to produce a mix that is as strong as Portland cement, with as little alkaline activator and granulated blast furnace slag as possible.

EXPERIMENTAL PART

Fly ash. The fly ash was supplied from the dry ash removal unit of EVRAZ ZSMK's Novokuznetsk power plant. This plant was chosen because of the widespread use of Kuznetsky coal-fired TPPs throughout the Russian Federation. We packed the samples in airtight containers to preserve the natural humidity.

The particle density was determined by the pycnometric method, the residue on the sieve by sieving without water washing, the specific surface by the Blaine air permeability method, the loss on ignition by heating the samples in crucibles at 850 °C and the moisture by calcination to constant mass.

The chemical composition of the fly ash (Table 1) was determined by X-ray fluorescence method. The chemical composition of the ash is low calcium, low sulphate (class F to ASTM C618).

Granulated blast furnace slag. Granulated blast furnace slag produced by BF-5 (Blast Furnace Shop No. 5) was sampled from a stack located at "Novolipetskii metallurgicheskii kombinat" PJSC (PJSC NLMK), Lipetsk. After sampling, the slag was dried to constant weight at (55±5) °C and milled on a 40 ML laboratory drum mill for 4 hours. The physical properties of ground granulated blast furnace slag were determined by the same methods as for the fly ash and are given in Table 1.

Table 1. Physical and chemical properties of the mixture components

Name of parameter	Actual data		Unit of measure
	TPP EVRAZ ZSMK, Kuznetsky UB	BF-5, PJSC "NLMK"	
1. Particle density	2.1	2.6	g/cm^3
2. Residual on sieve 008	1.5	8.0	%
3. Specific surface area	274.7	195.0	m^3/kg
4. Losses on ignition	1.1-1.5	4.5	%
5. Humidity	0.3	0.1	%
SiO_2	58.2	28.8	%
Al_2O_3	24.1	6.0	%
Fe_2O_3	7.4	0.4	%
CaO	1.7	52.1	%
MgO	0.8	7.6	%
$Na_2O + K_2O$	1.7	1.4	%
SO_3	0.8	–	%
loss on ignition	1.3	4.5	%

Liquid glass. For the experiments we used sodium liquid glass with a density of 2.47 g/cm^3.

Sodium hydroxide. NaOH was supplied by OOO "Omskreaktiv" in the form of granules, which were milled on an MG-1F mill to a size of less than 0.02 mm. In terms of purity, sodium hydroxide is pure for analysis, anhydrous.

Water. We used tap drinking water for the tests. The hydrogen index (pH) is 7.7, the content of soluble salts is 65 mg/dm^3, including SO4 ions 28.4 mg/dm^3 and chlorides 15 mg/dm^3.

The idea of the experiment was to prepare a binder based on ground blast furnace slag and fly ash activated with an alkaline component. The alkaline component consisted of a mixture of sodium hydroxide and an aqueous solution of sodium silicate (liquid glass).

We conducted the first experiment to assess the effect of the ratio of fly ash to ground blast furnace slag at the same alkaline activator content, and the second one was a full factor experiment with a number of factors of 3.

The first cycle. We made compression strength specimens containing 4% sodium hydroxide (NaOH) and 25% Na_2SiO_3 aqueous solution - liquid glass (LG) as part of an experiment to evaluate the effect of the ratio of fly ash to ground blast furnace slag. For this purpose, we used FC20-6 cube moulds with dimensions of 20x20x20 mm. In order to prevent the binder from adhering to the mould, we used petrolatum as a release agent. The moulds and the metal plate that were used as the base of the moulds were heavily greased.

The first mixing step was the mixing of the dry ingredients (GGBFS and FA). Then we added an alkaline activator and did the final mixing with the addition of water in the amount corresponding to the normal density.

We filled the prepared mixture into the cubic moulds. In order to obtain a homogeneous distribution of the mixture over the mould, we used a vibrating table, VIBR-X-15, to compact it for 2 minutes. We placed the moulds with the material under study in the curing chamber KNT-1.

A day after moulding we demoulded the samples and placed them in a curing chamber for curing at 22 °C. After 7 days, we tested all the samples to determine the compressive strength on an IR 5081-5 press at a speed of 6 mm/min. The same steps were done for samples at 28 days of age.

The second cycle. We decided to use ground granulated blast furnace slag (GGBFS), sodium hydroxide (NaOH) and liquid glass (LG) as factors in a complete factor experiment. In addition, we prepared the composition to obtain values for the components corresponding to the middle of the interval of variation of the factors.

Table 2. Recipes for binder mixtures

No. of the composition	Content of mixture components, %				Water content per 250 g mixture without liquid glass, g
	Dry components		Alkaline activator		
	GGBFS	Fly Ash	NaOH	Liquid glass	
1	45	51	4	25	10.0
2	15	81	4	25	10.0
3	45	53	2	25	10.0
4	15	83	2	25	10.0
5	45	51	4	15	25.0
6	15	81	4	15	25.0
7	45	53	2	15	25.0
8	15	83	2	15	25.0
9	30	67	3	20	18.5

The production of the samples was conducted in the same way as in the description of the first test cycle.

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RESULT AND DISCUSSION

The results of the first test cycle (Fig. 1) show a steady increase in the strength of the binder as the GGBFS content increases up to 90%, after which a decrease in strength is observed.

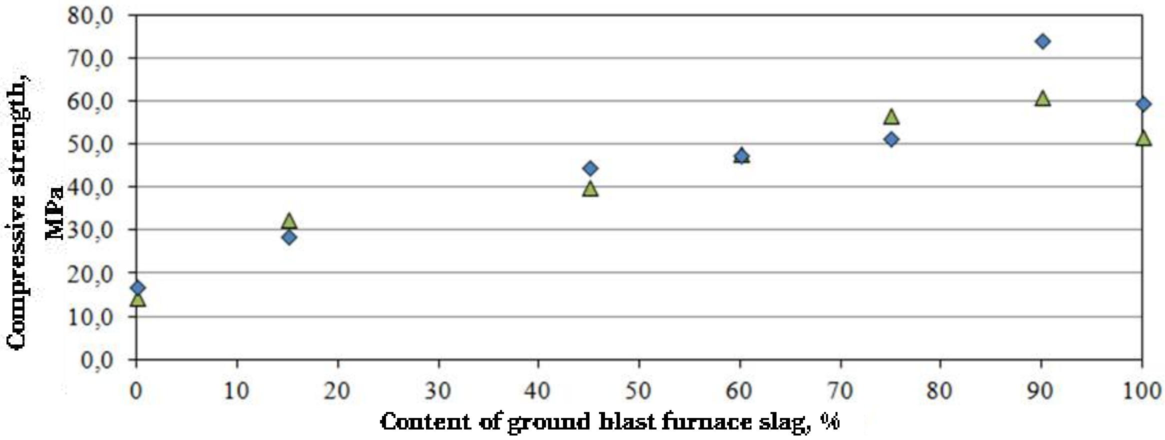

Fig. 1. Dependence between compressive strength and content of ground blast furnace slag (fly ash):
▲ - on the 7th day; ◆ - on the 28th day

The fall in strength with an increase above 90% of GGBFS content is probably due to the absence of voids in the material structure, which allow new joints to form without a significant increase of internal stresses. At the same time, a potentially suitable strength of the binder [22] is already achieved with an GGBFS content of 15 % and this strength increases practically linearly by 5 MPa for every 10 % of GGBFS. Considering the logistics and the need to grind granulated blast furnace slag, we decided to examine a minimum permissible amount of GGBFS in the second cycle of experiments. The results of the second cycle compressive strength tests of the binder samples after curing are shown in Table 3.

Table 3. Test results of the second cycle of tests

Curing time	Compressive strength, MPa								
	No. of the composition								
	1	2	3	4	5	6	7	8	9
7 days	52.3	32.3	24.4	2.,4	35.1	8.7	10.0	8.9	16.2
28 days	44.7	28.6	40.9	33.1	29.0	12.8	29.4	12.8	30.1

We used the theory of experiments planning. This allowed us to develop a formula to predict the ultimate strength of the resulting mixture when varying the factors and taking into account their combined effect on the 7th day ($R^2 = 0.99$):

$$R_{\mathrm{Comp7}} = 22.12 + 6.30 \cdot X_{\mathrm{S}} + 7.97 \cdot X_{\mathrm{N\,aOH}} + 8.45 \cdot X_{\mathrm{LG}} + 5.30 \cdot X_{\mathrm{S}} \cdot X_{\mathrm{NaOH}} - \text{¿}$$
$$-0.54\, X_{\mathrm{S}} \cdot X_{\mathrm{LG}} + 1.75 \cdot X_{\mathrm{NaOH}} \cdot X_{\mathrm{LG}} - 1.03 \cdot X_{\mathrm{S}} \cdot X_{\mathrm{NaOH}} \cdot X_{\mathrm{LG}}$$

where *Xi* is the content of the mixture component specified in the index.

On the 28th day (R^2-0.98):

$$R_{\mathrm{Comp28}} = 28.91 + 7.08 \cdot X_{\mathrm{S}} + 0.11 \cdot X_{\mathrm{NaOH}} + 7.90 \cdot X_{\mathrm{LG}} + 1.00 \cdot X_{\mathrm{S}} \cdot X_{\mathrm{NaOH}} - 1.10\, X_{\mathrm{S}} \cdot X_{\mathrm{LG}} - \text{¿}$$
$$-0.03 \cdot X_{\mathrm{NaOH}} \cdot X_{\mathrm{LG}} + 1.08 \cdot X_{\mathrm{S}} \cdot X_{\mathrm{NaOH}} \cdot X_{\mathrm{LG}}$$

In general, we found that the most significant influence on the strength of the final geopolymer is the content of ground granulated blast furnace slag and sodium silicate solution. The impact of sodium hydroxide, on the other hand, is favourable in the early stages of hardening, but an increase in concentration above 3% seems to lead to material degradation [19] over time (compositions 1, 2 and 5).

CONCLUSION

1) Potentially suitable strength of the hybrid binder can be achieved by including ground granulated blast furnace slag of 15%. Without the use of ground granulated blast furnace slag, this cannot be achieved without heat and humidity treatment. The strength index increases linearly by 5 MPa for every 10 % of the input additive.

2) In the presence of sodium hydroxide, strength gain is accelerated during the first 7 days of curing, but additive concentrations above 3% lead to degradation of the material over time.

3) To assess a wide range of physical-chemical properties of binders under alkaline activation it is recommended to conduct additional studies with ash-and-slag mixtures of other composition from power plant dumps as well as to conduct full factor experiments.

REFERENCES

1. **Vojtko, A.R., Legkota, E.V. & CHenskaya, A.M.** (2022) Severe recession and territorial polarization of investments, *Molodoj uchyonyj goda 2022: sbornik statej II Mezhdunarodnogo nauchno-issledovatel'skogo konkursa*, *Penza, 25 maya* 2022 *g*. Penza, pp. 75–78 (in Russian).
2. **Iguminova, V.A. & Rekhovskaya, E.O.** (2021) Recycling of waste from TPP plants, *Materialy XIX Vserossijskoj nauchno-prakticheskoj konferencii*, *Omsk, 9–11 nov. 2021 g.* Omsk: Omskij gos. tekhn. un-t, pp. 84-87 (in Russian).
3. **Fomina, E.V. & Fransishko De Kastro, B.K.** (2020) Ecological aspects of the use of steelmaking slag, *Racional'noe ispol'zovanie prirodnyh resursov i pererabotka tekhnogennogo syr'ya: fundamental'nye problemy nauki, materialovedenie, himiya i biotekhnologiya*, *Alushta-Belgorod, 1-5 iunya 2020 g.* Belgorod, pp. 290–295 (in Russian).
4. **Eroshkina, N.A., Tymchuk, E.I. & Korovkin, M.O.** (2015) Structure formation of geopolymers, *Molodoj uchenyj*, 87, pp. 123–126 (in Russian).
5. **Davidovits, J.** (1991) Geopolymers - Inorganic polymeric new materials, *J. Therm. Anal.*, 37(8), pp. 1633–1656.
6. **Singh, N.B.** (2018) Fly ash-based geopolymer binder: A future construction material, *Minerals*, 8(7), p. 299. DOI: 10.3390/min8070299.
7. **John, S.K., Nadir, Y. & Girija, K.** (2021). Effect of source materials, additives on the mechanical properties and durability of fly ash and fly ash-slag geopolymer mortar: A review, *Construction and Building Materials*, 280, pp. 1-32. DOI: 10.1016/j.conbuildmat.2021.122443.
8. **Kaya, M. et al.** (2022) Influence of micro Fe_2O_3 and MgO on the physical and mechanical properties of the zeolite and kaolin based geopolymer mortar, *J. Build. Eng.*, 52, pp. 104-443. DOI: https://doi.org/10.1016/j.jobe.2022.104443.
9. **Ma, B. et al.** (2022) The influence of calcium hydroxide on the performance of MK-based geopolymer, *Construction and Building Materials*, 329, pp. 127-224. DOI: 10.1016/j.conbuildmat.2022.127224.
10. **Liew, Y.M. et al.** (2016) Structure and properties of clay-based geopolymer cements: A review, *Prog. Mater. Sci.*, 83, pp. 595–629. DOI: https://doi.org/10.1016/j.pmatsci.2016.08.002.
11. **Lekshmi, S. & Sudhakumar, J.** (2022) An assessment on the durability performance of fly ash-clay based geopolymer mortar containing clay enhanced with lime and GGBS, *Clean. Mater.*, 5, pp. 100-129. DOI: 10.1016/j.clema.2022.100129.

12. **Tekin, I.** (2016) Properties of NaOH activated geopolymer with marble, travertine and volcanic tuff wastes, *Construction and Building Materials*, 127, pp. 607–617. DOI: 10.1016/j.conbuildmat.2016.10.038.
13. **Liu, M. et al.** (2022) Reusing recycled powder as eco-friendly binder for sustainable GGBS-based geopolymer considering the effects of recycled powder type and replacement rate, *J. Clean. Prod*., 364, pp. 132656. DOI: 10.1016/j.jclepro.2022.132656.
14. **Eroshkina, N.A., Korovkin, M.O. & Korovchenko, I.V.** (2015) Technology for obtaining geopolymer binder based on igneous rocks, *Molodoj uchenyj*, 87, pp. 120–123 (in Russian).
15. **Wu, X., Shen, Y. & Hu, L.** (2022) Performance of geopolymer concrete activated by sodium silicate and silica fume activator, *Case Stud. Constr. Mater.*, 17, pp. 501-513. DOI: https://doi.org/10.1016/j.cscm.2022.e01513.
16. **Petrus, H.T.B.M. et al.** (2021) Green geopolymer cement with dry activator from geothermal sludge and sodium hydroxide, *J. Clean. Prod*., 293, pp. 126-143. DOI: https://doi.org/10.1016/j.jclepro.2021.126143.
17. **Pu, S. et al.** (2022) Water resistance of fly ash phosphoric acid-based geopolymer, *Dev. Built Environ*., 12, pp. 1-14. DOI: https://doi.org/10.1016/j.dibe.2022.100093.
18. **Yusuf, G. Adewuyi.** (2021) Recent Advances in Fly-Ash-Based Geopolymers: Potential on the Utilization for Sustainable Environmental Remediation, *ACS Omega*, 6(24), pp. 15532–15542. DOI: https://doi.org/10.1021/acsomega.1c00662.
19. **Efremov, A.N., Haustova, V.V. & Bukina, D.Yu.** (2018) Composite slag-alkaline binders based on sodium hydroxide, blast furnace granulated slag and ash and slag waste from thermal power plants, *Vestnik Donbasskoj nacional'noj akademii stroitel'stva i arhitektury*, 4-2(132), pp. 177–182 (in Russian).
20. **San Nicolas, R.V.R., Walkley, B. & van Deventer, J.S.J.** (2017) Fly ash-based geopolymer chemistry and behavior, *Coal Combustion Products (CCPs): Characteristics, Utilization and Beneficiation*, pp. 185–214. DOI: https://doi.org/10.1016/B978-0-08-100945-1.00007-1.
21. **Wongpa, J. et al.** (2010) Compressive strength, modulus of elasticity, and water permeability of inorganic polymer concrete, *Mater. Des*., 31(10), pp. 4748–4754. DOI: 10.1016/j.matdes.2010.05.012.
22. **Diaz, E.I., Allouche, E.N. & Eklund, S.** (2010) Factors affecting the suitability of fly ash as source material for geopolymers, *Fuel*, 89(5), pp. 992–996. DOI: 10.1016/j.fuel.2009.09.012.

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