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RESEARCH ON THE STRUCTURE FORMATION PROCESSES IN THE SYSTEM "BLAST FURNANCE SLAG – WASTEPAPER SLUDGE ASH"

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Concrete production is one of the largest consumers of natural non-metallic materials. To mitigate the environmental impact associated with cement production The use of wastepaper sludge ash (WSA) from paper recycling is a new promising direction for saving fuel, energy, and natural resources in cement and concrete production, aimed at reducing the proportion of clinker in cement by replacing part of the cement with supplementary cementitious materials. This approach aligns with the priority principles of uniform and sustainable industry development aimed at creating environmentally friendly, low-energy-consuming technologies. This study is dedicated to investigating the properties of composite systems with different proportions of blast furnace granulated slag and wastepaper sludge ash. Test results show that samples with 70 % WSA achieve the highest early strength (2.23 MPa flexural, 7.6 MPa compressive). Later, samples with a 70 : 30 BFS : TAW ratio exhibit the highest strength (38.3 MPa compressive, 4.6 MPa flexural) due to predominant hydro silicate hydration. The composite system forms CSH(B) hydro silicates and calcium hydro aluminate C_4AH_{13}, reacting with WSA gypsum to form calcium hydro sulphoaluminate $C_3A·3CaSO_4·32H_2O$ during initial hydration.

Key words: Granulated Blast Furnace Slag (GBFS); paper production waste; Wastepaper Sludge Ash (WSA); composite binders; hardening activation; supplementary cementitious materials.

Introduction

The balanced use of natural resources and production waste plays a crucial role in achieving sustainable development of the state and society. In contemporary conditions, this serves as a guarantee for preserving the stability of the eco-economic system across all industrial sectors, including construction.

A primary type of waste from paper production, known as paper mill sludge, is formed as a result of secondary processing of wastepaper. Paper mill sludge constitutes a significant portion of industrial waste, with the International Energy Agency (IEA) estimating global production at approximately 11 million tons annually. The annual volume of sludge generated at Ukraine's largest paper mill, the Kyiv Cardboard and Paper Mill, which processes about 30 % of the nation's wastepaper, amounts to around 45 thousand tons. Most of the waste from paper production is buried in landfills, posing a significant environmental problem by polluting the atmosphere and underground water sources.

Thus, the accumulation of a large volume of paper production waste requiring proper management presents a serious issue. This has led to the search for effective environmentally and economically sound methods of disposal and recycling (Monte, 2009; Bajpai, 2015; Cusido, 2015; Di Fraia, 2022; Lou, 2012).

To mitigate the environmental impact associated with cement production and the constant depletion of natural resources, there is a need to develop alternative binding materials to make the concrete industry environmentally sustainable. Traditionally, granulated blast furnace slag is introduced into the composition of Portland cement for this purpose, however nowadays it became scarce due to destruction of biggest iron and steel production facilities in Ukraine. The use of thermally activated wastepaper sludge (or wastepaper sludge ash – WSA, as predominantly referred in scientific sources) from paper recycling is a new promising direction for saving fuel, energy, and natural resources in cement and concrete production, aimed at reducing the proportion of clinker in cement by replacing part of the cement with supplementary cementitious materials. In investigating the partial replacement of cement in concrete mixes with thermally activated waste from the paper industry, the potential for their use as additional cementitious materials was established, resulting in reduced Portland cement consumption (Frias, 2001; Frias, 2011; Frias, 2015; Banfill, 2007; Fava, 2011; Doudart de la Grée, 2018; Bikila, 2021; Solahuddin, 2021; Ahmad, 2013). This approach aligns with the priority principles of uniform and sustainable industry development aimed at creating environmentally friendly, low-energy-consuming technologies.

However, despite various methods of utilizing and recycling paper mill sludge and considering the large volume generated, the search for new effective methods of utilizing paper production waste remains a primary challenge of high global priority (Mozafari, 2006; Mozafari, 2009; Ishimoto, 2000; Liu, 2020). Current study is dedicated to evaluating the properties of composite systems with different proportions of granulated blast furnace slag and wastepaper sludge ash.

Materials and Methods

Physical and mechanical testing of cements was conducted in accordance with national and international standards (EN 196-9-2007, DSTU B V.2.7-185:2009, DSTU B V.2.7-187:2009), including the determination of normal density of cement paste, setting times, and flexural and compressive strength.

The study utilized wastepaper sludge ash collected after incineration of paper mill sludge as alternative fuel in patented furnace at the Kyiv Cardboard and Paper Mill. Main properties of WSA are presented in previous research (Hunyak, 2022). Granulated blast furnace slag from ArcelorMittal Kryvyi Rih was used as an active mineral additive.

Results and discussion

Given the widespread use of blast furnace granulated slag-added Portland cements in concretes, the influence of thermally activated waste on the hydration processes of blast furnace granulated slag was investigated.

It is known (Sobol, 2019) that the hydraulic activity of granulated slags is determined by their glassy structure, characterized by metastability. Therefore, the hydraulic activity of blast furnace granulated slag manifests only when activated by an alkaline, sulfate, or mixed mechanism. Interaction with hydration activators disrupts the thermodynamically unstable state of slag glass, triggering hydration processes.

The study revealed (Sobol, 2020; Hunyak, 2022) that thermally activated wastepaper comprises hydraulic active phases, primarily high-basic calcium aluminates C_3A and $C_{12}A_7$, calcium silicate β-C2S, a small amount of free lime CaO, and a regulating complex additive containing 7.0 % $CaSO_4 \cdot 2H_2O$ and 1.0 % tartaric acid.

Considering the chemical-mineralogical composition and hydraulic activity of WSA, its effectiveness in activating the hardening of blast furnace granulated slag was examined. To study the influence of the composition ratio of the blast furnace granulated slag – WSA composite system on its physical and mechanical properties, samples of 2×2×8 cm were formed with a ratio of 1 : 0 and cured under normal conditions. Test results are presented in Table.

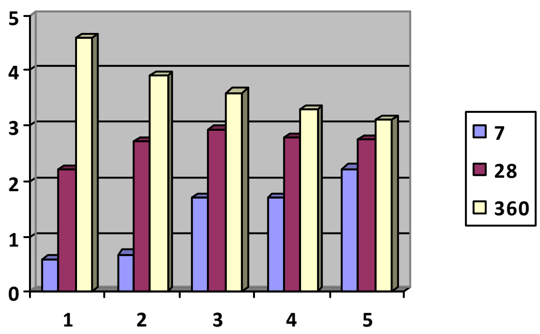
The results showed that as the content of thermally activated waste in the system increases, the water demand of the binder also increases. Additionally, there is a clear relationship between the WSA content and the setting time of the binding system: with an increase in WSA content, the setting time decreases. For example, at a blast furnace granulated slag: WSA ratio of 70 : 30, the initial setting time is 45 minutes, and the final setting time is 1 hour 40 minutes, whereas for a ratio of 30 : 70, the setting times are 22 and 45 minutes, respectively.

Effect of composition on the physico-mechanical properties of the binding system

No.	Composition of the binder system, mass %		Setting time, hour : min		Soundness	Standard consistency, W/B
	GBFS	WSA	Initial	Final		
1	70	30	0:45	1:40	No	0,28
2	60	40	0:35	1:15	No	0.30
3	50	50	0:30	1:00	No	0.32
4	40	60	0:26	0:55	No	0.36
5	30	70	0:22	0:45	Yes	0.39

Since WSA contains some amount of free CaO, the tendency of the composition to expand during hardening was also determined by steam curing the samples in a Le Chatelier bath. The results indicate that only when the GBFS : WSA ratio exceeds 40 : 60 does expansion exceed 10 mm, as permissible by (EN 196-9).

It has been established that samples with the maximum content of WSA – 70 wt. % exhibit the highest early strength of 2.23 MPa in flexure and 7.6 MPa in compression. This is attributed to the rapid hydration of aluminate phases within WSA, which contributes to strength during early-stage structure formation. However, the highest strength parameters, both in compression (38.3 MPa) and especially in flexure (4.6 MPa), at later hydration stages, when the predominant solidification mechanism is of the hydrosilicate type, are demonstrated by samples with a ratio of FGS : WSA = 70 : 30 (Fig. 1).



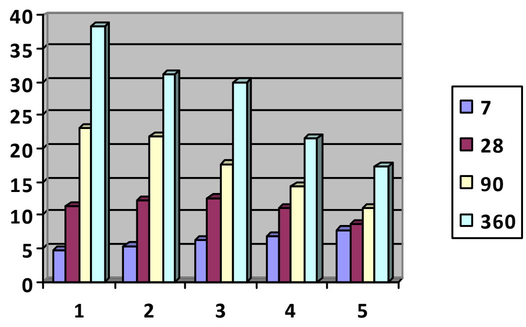


Fig. 1. Ultimate tensile (left) and compressive (right) strength, MPa

The obtained results and their interpretation indicate the effectiveness of using WSA to activate GBFS, which occurs through sulfate and partially alkali mechanisms. As demonstrated by X-ray diffraction studies (Fig. 2), the main hydrated phases in the compositional system of 70 wt. % GBFS and 30 wt. % WSA are calcium silicate hydrates of the CSH(B) composition, calcium hydroaluminates C_4AH_{13}, which, interacting with gypsum present in WSA, form ettringite $C_3A\ 3CaSO_4{\cdot}32H_2O$ during the initial hydration period. Free CaO, present in WSA, rapidly converts to $Ca(OH)_2$, which eventually carbonates over time. Another characteristic feature of this system is the carbonation of calcium hydroaluminates to form calcium hydroxyaluminates of the composition $4CaO{\cdot}Al_2O_3{\cdot}CO_2{\cdot}12H_2O$.

In the microphotographs of the FGS – WSA system, hydrated for 28 days (Fig. 3), clusters of large crystals of calcium aluminosilicates present in the slag component are observed.

As a result of the combined hydration of GBFS and WSA, fibrous crystals of calcium hydrosilicates and elongated prismatic crystals of ettringite are observed, which is confirmed by the results of X-ray phase analysis and correlates well with the results of physico-mechanical tests of the binder composite system GBFS – WSA.

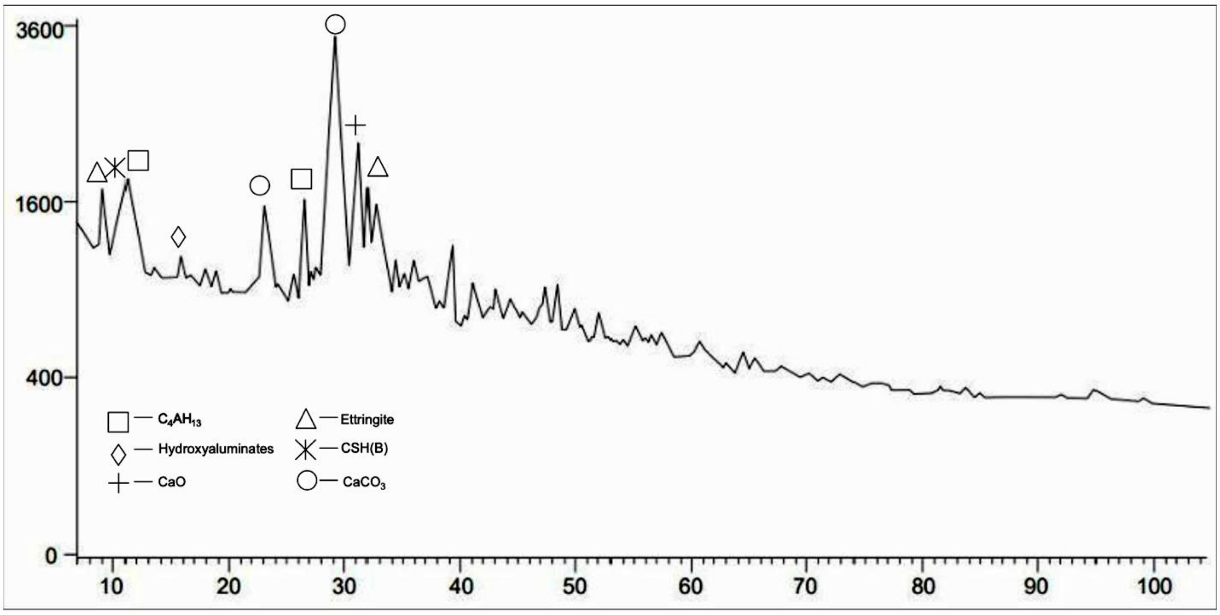


Fig. 2. XRF of the hydrated composite system with a composition of 70 wt. % GBFS + 30 wt. % WSA at the age of 28 days

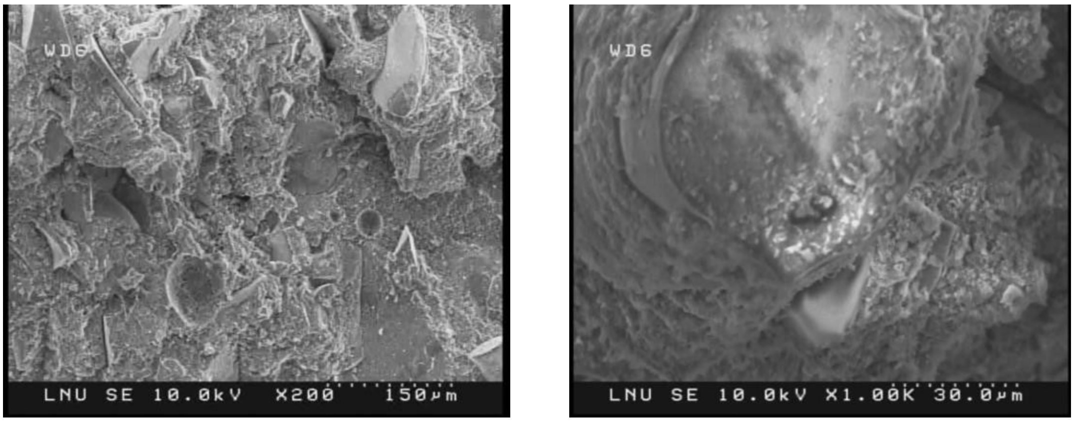


Fig. 3. Microstructure of the hydrated composite system with a composition of 70 wt. % GBFS + 30 wt. % WSA at the age of 28 days

Thus, the effectiveness of the combined use of blast furnace slag and thermo-activated waste in binder systems is established at the optimal ratio of GBFS : WSA = 70 : 30. The activation of the slag component by wastepaper sludge ash and the synergistic effect manifested during their hydration ensure relatively high physico-mechanical properties of the hardened composite.

Conclusions

Research has demonstrated the effectiveness of utilizing thermo-activated wastepaper within the binder composite system "blast furnace slag – wastepaper sludge ash", through the activation of slag component system hardening and the synergistic effect, which facilitates the formation of additional structurally active phases during their combined hydration.

It has been established that thermo-activated waste in the investigated system "GBFS – WSA" serves as an additional cementitious material, allowing for a reduction in the proportion of the most energy-intensive clinker component of cement, aligning with contemporary trends in conserving fuel and energy resources by extensively incorporating industrial waste into construction. Developed composite binder may be potentially utilized in renders, mortars, soil stabilization, lean roller-compacted and low-strength conventional concrete after further valorization in specific applications.

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ДОСЛІДЖЕННЯ ПРОЦЕСІВ СТРУКТУРОУТВОРЕННЯ В СИСТЕМІ "ДОМЕННИЙ ГРАНУЛЬОВАНИЙ ШЛАК – ТЕРМОАКТИВОВАНІ ВІДХОДИ ПАПЕРОВОГО ВИРОБНИЦТВА"

Цементна промисловість є одним із основних джерел викидів вуглекислого газу – вона продукує близько 7 % від усіх викидів парникових газів. Щоб усунути вплив на навколишнє середовище, пов'язаний із виробництвом цементу, потрібно розробити альтернативні в'яжучі речовини, щоб бетонна промисловість стала стійкою в екологічному сенсі. Традиційно з цією метою до складу портландцементу вводять доменні гранульовані шлаки. Використання термооброблених відходів паперопереробки є новим перспективним напрямом економії паливо-енергетичних та природних ресурсів під час виробництва цементу і бетону, що передбачає зменшення частки клінкеру в цементі за рахунок заміни частини цементу додатковими цементуючими матеріалами.

Під час дослідження ефективності використання термоактивованих відходів як додаткових цементуючих матеріалів вивчено властивості композиційних систем з різним співвідношенням доменного гранульованого шлаку та термоактивованих відходів. Результати фізико-механічних випробувань зразків композиційної системи "ДГШ – ТАВ" показали, що найвищої ранньої міцності – 2,23 МПа на згин та 7,6 МПа на стиск досягають зразки із максимальним вмістом ТАВ – 70 мас. %. Це пояснюється швидкою гідратацією алюмінатних фаз у складі ТАВ, що забезпечує міцність під час раннього структуроутворення. Проте найвищими показниками міцності як на стиск (38,3 МПа), так і, особливо, на згин (4,6 МПа) у пізні терміни гідратації, коли переважає гідросилікатний тип тверднення, характеризуються зразки зі співвідношенням ДГШ : ТАВ=70 : 30.

Дослідження фазового складу розробленої композиційної системи свідчать про утворення гідросилікатів CSH(B), а також гідроалюмінатів кальцію C_4AH_{13}, які, взаємодіючи з гіпсом, що входить до складу ТАВ, утворюють гідросульфоалюмінат кальцію $C_3A{\cdot}3CaSO_4{\cdot}32H_2O$ вже в початковий період гідратації.

Ключові слова: доменний гранульований шлак; відходи паперового виробництва; макулатурний скоп; в'яжучі композиції; активізація тверднення; додаткові цементуючі матеріали.