

EVALUATION OF THE USABILITY OF THE ALKALI ACTIVATED INDUSTRIAL WASTES AS A MATRIX AND SUPPORT OF PHOTOCATALYSTS

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Abstract

The aim of this study was to evaluate the possibility of the metallurgical wastes (slags and fly ash) utilization as a support for photocatalytically active composites. Metallurgical slags (MS) represent large volume group of by-products originated during the metallurgical production processes. The fly ash (FA) is the group of the wastes coming from the power plants, which are also part of the big cast iron and steel production plants. Although several applications of MS and FA already exist, non-negligible part is still stored in the landfills and thus the searching for new applications of these wastes is on high demand. Alkali activation of MS and FA represents one of the possibilities of the re-utilization of these wastes, which enables the application of these materials as the inorganic binders in building industry. The combinations of the photocatalysts with cement based materials are intensively studied with the aim of their utilization for the photocatalytic cleaning of the air. In present work, the alkali activated MS was tested as the matrix for the photocatalytically active composite kaoline/TiO₂ and the alkali activated mixture of MS+FA was evaluated as a support the deposition of TiO₂ layer. The photodegradation activity of prepared samples against NO_x was tested. The results identified the application of TiO₂ layer on the surface of alkali activated mixture MS+FA as favourable with respect to NO conversion.

Keywords: Slag, alkali activation, TiO₂, photocatalysts, photodegradation

1. INTRODUCTION

High amount of the wastes and by-products is produced by the metallurgy and energy industry and the building industry is the biggest consumer of these materials [1]. The blast furnace slag (BFS) and fly ash (FA) are widely used as the components of blended cements. Heavy aggregates produced from slowly cooled slags used for the road construction is the other example of the possible utilization of the by-products from the metallurgy. The requirement for the utilization of these materials as the alternative inorganic binders is high amount of Al₂O₃ and SiO₂ in amorphous phase, which assure the ability of the so called latent hydraulic activity (LHA) [2]. Latent (hidden) hydraulic properties of these materials can be evoked by the addition of the suitable alkali activator and so called Alkali Activated Materials (AAM) originated. Latent hydraulic properties of the granulated blast furnace slag (GBFS) and fly ash are usually induced by the addition of the water glass.

The hardened products matured in moist environment could exhibit even better properties (mechanical properties, chemical resistance) in comparison to the products prepared by the hydration of Ordinary Portland cement (OPC). OPC is an excellent hydraulic binder but its production is energetically demanding due to the necessity of the calcination of the raw materials in rotational furnace, other negative environmental aspects is the production of the high amount of CO₂ [3]. The tuning of the alkali activation process of GBFS and FA is frequently studied in a number of scientific reports dealing with inorganic binders [4,5]. The result of the alkali activation is the formation of new phases, which have the dominant effect on the final mechanical properties, and chemical resistance of the hardened samples [6]. The properties of the final product are influenced also

by the type of the alkali activator as well as by the process of the mixing of the tested AAM admixtures with alkali activator. The preparation of the tiles, curbs or the protection tiles placed at the road edges as well as the noise protective barriers represent the already tested real application of the alkali activated materials.

The air pollution is a serious problem and enormous effort is put to develop the procedures for the decreasing of its level. One of the often researched ways for the elimination of the hazardous substances from the air is their photocatalytic degradation [7]. Since the buildings, roofs, noise barriers but also the surface of the roads are in direct contact with the air, the utilization of the photocatalytic degradation process of the pollutants running on the surfaces of these construction parts represent an elegant way to improve the air quality. The most studied photocatalyst is TiO₂ and its utilization in the building parts based on Portland cement has been already explored by many researchers for example [8-10]. The utilization of AAM as the support of photocatalytically active materials is not researched in such range as the materials based on OPC as the binder.

The aim of this work was to evaluate the possibility to utilize photocatalytically active materials in the combination with the hardened matrix based on the AAM. Two different approaches for the combination of TiO₂ photocatalyst were tested. In the first approach, photocatalytically active composite kaoline/TiO₂ was used as the admixture of GBFS. And this mixture was activated with the sodium metasilicate and let to harden in the moist environment. In the second approach, TiO₂ in the form of colloid sol was used to cover the surface of already hardened samples produced by the alkali activation of the mixture of GBFS and FA using water glass. The photocatalytic activity of prepared samples was tested by the photodegradation of NO₂.

2. MATERIALS AND METHODS

Two different approaches of the TiO₂ combination with LHA materials were tested. The first approach was based on the addition of kaoline/TiO₂ (KATI) composite in an amount of 15 and 25 wt.% into the powder GBFS and further mixed with granules of sodium metasilicate (NMS). The water was then added to this dry mixture and originated paste was formed into the mould made of steel and let to mature 24h in moist environment (25 °C, 99% RH). After 24 h the samples were unmoulded and stored in the moist environment for selected time period (2, 7, 28 and 56 days). The composition of the samples is shown in **Table 1**. Since the composite KATI is based on the TiO₂ particles anchored on the surface of the kaolinite particles the samples containing only calcined kaoline (MK) were prepared in the same way and labelled as MK15 and MK25. The samples in a form of small cubes (20x20x20mm) as well as in the form of tiles (100x50x10mm) were prepared for the compressive strength tests and photocatalytic experiments.

Table 1 Composition of the GBFS samples

Sample	MK	KATI66	FA	GBFS	Na ₂ O	Water to solid ratio
	(g)	(g)	(g)	(g)	%	
GBFS	0	0	0	300	2.5 / 5	0.31
MK15	45	0	0	255		0.34
MK25	75	0	0			0.36
KATI15	0	45	0			0.34
KATI25	0	75	0			0.36
GBFS_FA20	0	0	60	240	5	0.30
GBFS_FA40	0	0	120	180		0.30

The second approach comprises the samples based on the mixture of GBFS and FA prepared in the same way as the samples previously described with the exception that the mixture did not contain TiO₂ photocatalyst. The samples were labelled GBFS_FA20 and GBFS_FA40 where the number signalizes the FA content, the composition of the samples is shown in **Table 1**. After 28 days of maturation in moist environment, the samples in a form of tiles were further stored in laboratory conditions (25 °C, 30% of RH) for additional 14 days to let them dry slowly. After that, the TiO₂ suspension was applied on the surface of the tiles by the dipping of the tile into the TiO₂ suspension for 10s. After that, the sample was let to dry for additional 4h. Then the samples were thermally treated in a muffle furnace for 2h at 450 °C. The whole process was applied three times.

The compressive strength test was performed for the samples in a form of cubes after their maturation for 2, 7, 28 and 56 days long hydration on the compression strength tester Compact 20/160 (Brio Hranice).

Apparatus and the conditions used for NO photodegradation experiment are in agreement with requirements given by international standard ISO 22197-1:2007. The scheme of the apparatus is shown in **Figure 1**.

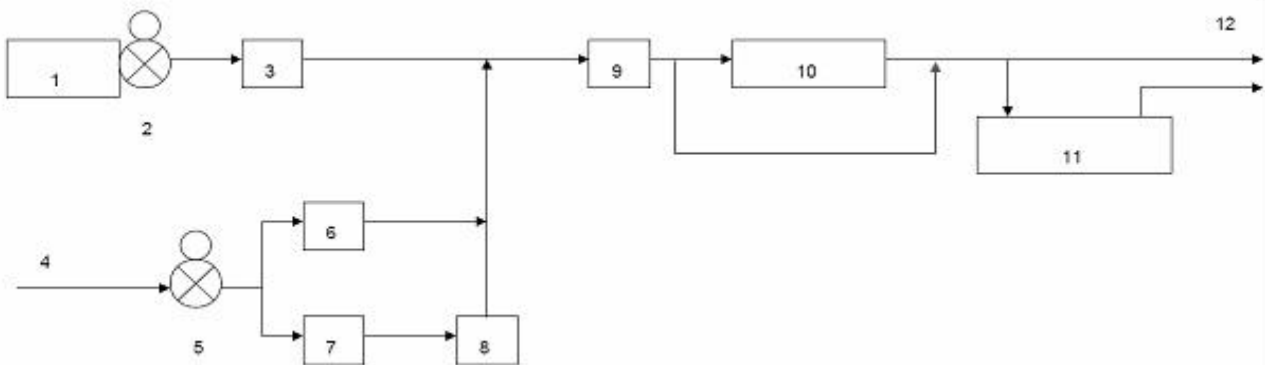


Figure 1 The scheme of the apparatus used for the NO_x photodegradation test (1. Gas cylinder with mixture of N₂ + NO, 2., 5. Reducing valves; 3., 6., 7. Mass flow controller, 4. Inlet of the pressurized air, 8. Glass wash bottle, 9. The cell for the RH measurement, 10. Photoreactor with UV lamp, 11. NO_x analyser, 12. Outlet of the gas mixture)

NO was used as a model pollutant during the experiment and its initial stream dosed using mass flow controllers was mixed with air to give the final concentration 1.2 ppm. HORIBA APNA-370 analyzer was used for the detection of NO concentration. The flow rate of the inlet gas mixture through the reactor was 3 l·min⁻¹. OSRAM EVER SUN L40W/79K tube was used as a source of UV irradiation during the photodegradation tests. The UV light intensity (measured at 356 nm) was 10 W·m⁻². The relative humidity was kept at the value 49.7 ± 0.3 % during the measurement. The experiments were performed in shortened 60 min long irradiation period.

3. RESULTS

The effect of the amount of Na₂O in the activator on the compressive strength of the samples is shown in **Figure 2**. Application of the activator with 2.5 wt.% of Na₂O to GBFS let to develop the compressive strength value close to 80 MPa after 58 days long hydration. In the case of alkali activated mixtures of GBFS with MK or KATI composite the compressive strength reached very low values, which did not exceed 4 MPa (**Figure 2a**), the development of the compressive strength was the same for all of the tested samples regardless the type of the admixture used. Increasing of the Na₂O amount to 5 wt.% caused the formation of the samples with obviously higher values of compressive strength as evident from **Figure 2b**. Again the highest compressive strength around 80 MPa after 58 days of hydration was achieved for pure GBFS followed by the sample of GBFS with 15 wt.% of KATI admixture which reached approximately 40 MPa after the 58 days long hydration.

By the comparison of the compressive strength values obtained for the samples with MK and KATI admixtures (**Figure 2b**) the positive effect of the TiO_2 in the KATI composite was observed (**Figure 2b**). Lower amount of the admixtures is preferable for achieving of the higher compressive strength values (compare the series MK15 and MK25 and KATI15 and KATI25 in **Figure 2b**). The addition of the FA to the GBFS let to form the samples with obviously higher compressive strength, in comparison to pure GBFS, as evident from **Figure 3**. These mixtures were used for the preparation of the samples for which the TiO_2 was applied in a form of thin layers.

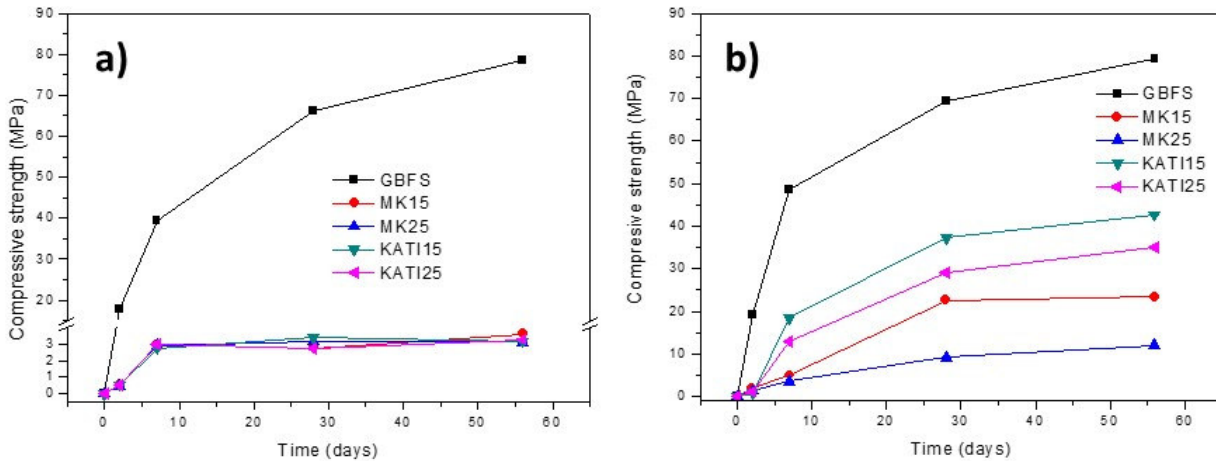


Figure 2 The time evolution of the compressive strength of the samples activated with the sodium silicate in amount carrying a) 2.5 wt.% of Na_2O and b) 5 wt.% of Na_2O

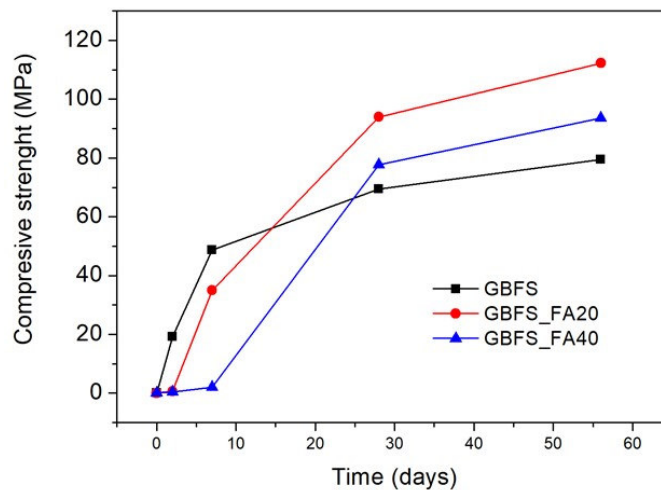


Figure 3 The time evolution of the compressive strength of the GBFS mixtures with FA

The degree of NO conversion caused by 60 min long UV irradiation of the samples with the presence of photocatalytic active TiO_2 is shown in **Figure 4**.

The conversion of the NO is negligible for the series of the samples with KATI composite as evident from **Figure 4**. Activation of the GBFS+KATI mixture using higher amount of alkali activator carrying 5 wt.% of Na_2O caused higher NO conversion compared with the samples activated with sodium metasilicate carrying 2.5 wt.% of Na_2O as evident from **Figure 4**. Higher conversion for sample KATI_25 is related to higher content of TiO_2 in this sample.

Application of TiO₂ in a form of thin layers was responsible for the enhancement of NO conversion which reached approximately 6 % in the case of the tiles prepared from the mixture of 60 wt.% of GBFS and 40 wt.% of FA. The positive effect of higher amount of FA on the NO conversion was observed (**Figure 4**) and could be attributed to enhanced fixation of Na⁺ ions in hydration products originated in the presence of FA.

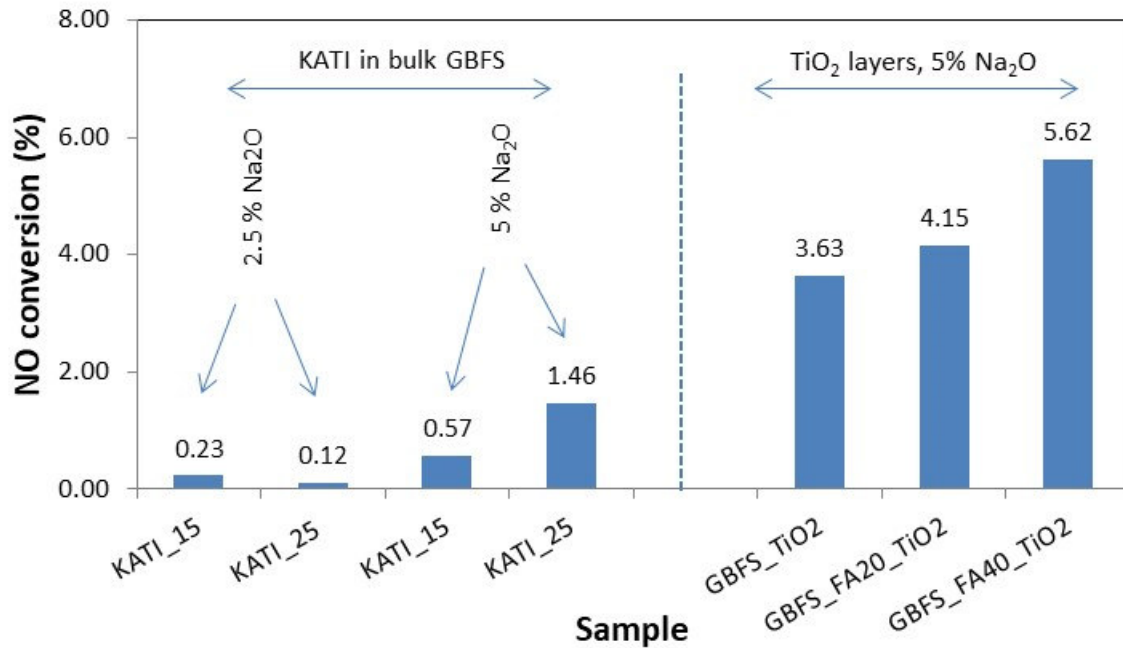


Figure 4 Comparison of the degree of NO conversion for the samples with composite KATI and the samples of tiles with the TiO₂ applied as the layer

4. CONCLUSION

The samples of alkali activated granulated blast furnace slags and its mixtures with i) calcined kaoline, ii) photocatalytically active composite KATI and iii) fly ash were prepared. The compressive strength values of the alkali activated mixtures of GBFS with MK and KATI revealed the importance of higher amount of alkali activator for higher strength of the mixtures with KATI. The positive effect of the TiO₂ presence was also observed. The addition of fly ash to the GBFS and subsequent alkali activation of the mixtures let to form hardened samples with even higher compressive strength. The tests of NO conversion revealed higher NO conversion for the samples with TiO₂ present in a form of thin layers. The positive effect of the amount of fly ash on the NO conversion was observed. The further experiments will be focused on the alkali activated samples with the different photocatalyst applied in a form of thin layers.

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