Surface modification of alkali-activated materials regarding durability

Lukas Prochazka[1], and *Adela* Brazdova[1*]

[1]Technical University of Ostrava, Faculty of Civil Engineering, Department of Building Materials and Diagnostics of Structures, 708 00 17. listopadu 2172/15, Czech Republic

Abstract. This paper deals with the possibility of applying a surface modification coating to hybrid alkali-activated materials based on granulated blast-furnace slag activated with disodium metasilicate anhydrous with partial replacement of silica fly ash and cement by-pass dust in the amounts of 15% and 15%. The selected coatings (epoxy and synthetic) were applied in two series - the first, deposited in the water after demolding, and the second, wrapped in foil. The strength of the materials, the thickness of the coating and the effect of scaling resistance were monitored in the experiment. The compressive strength of this mixture was around 68 MPa and the flexural strength was around 6.5 MPa after 28 days of curing. For the tensile strengths of the prepared composites, slightly higher strengths were obtained for the samples deposited in the plastic foil, with the strengths of both series being around 2.4 MPa. For the scaling resistance, the lowest weight losses were achieved for the specimens coated with synthetic coating, which is valid for both deposition methods.

1 Introduction

Globally, a total of 34.9 GtCO_2 of CO_2 emissions were produced in 2021 [1]. In the context of conventional concrete, it is generally estimated that global cement production corresponds to 5-10% of total CO_2 emissions [2, 3]. Furthermore, a 2004 article by [4] based on data from 1994 states that of the global average CO_2 emissions, a total of 1.381 Gt of cement and 1.126 Gt of CO_2 were produced, corresponding to 0.815 t CO_2 per tonne of cement [4, 5].

At present, with EU strategies to achieve climate neutrality by 2050, it is necessary to look for alternatives in terms of the sustainability of cement production. The production of Portland cement, namely the calcination of limestone at temperatures of 1400-1450 °C, produces 50-60 % of CO_2 (of the total concrete production) [6]. To reduce these emissions and thus contribute to the target, reductions can be achieved by using breakthrough technologies such as clinker replacement [7]. Alternatives to traditional Portland cement-based binders can be alkali-activated materials [8, 10, 11]. Several secondary raw materials such as granulated blast furnace slag (BFS), fly ash after denitrification (FAD) or cement bypass dust (CBPD) can be considered as alternatives [6, 11-16].

* Corresponding author: adela.brazdova@vsb.cz

BFS is produced as a secondary product of iron production in a blast furnace [13]. Due to the input materials, the slag has a high content of oxides (such as CaO, SiO_2, Al_2O_3 and MgO). Some studies have reported that these properties provide a significantly lower thermal conductivity of slag compared to metallic materials [11-13, 17]. In contrast, fly ash (FA) mainly consists of SiO_2, Al_2O_3 and Fe_2O_3, but can be divided according to CaO content into low-calcium (or siliceous) (FA) and high-calcium (or calcareous) (HCFA) [14]. When coal is burned, nitrogen oxides are released into the air. These can be reduced by Selective Catalytic Reduction (SCR) and Selective Non-Catalytic Reduction (SNCR) [15]. However, it has been reported that denitrification can lead to a deterioration in the properties of fly ash and thus to a worsening of cement (concrete) properties [15]. For this paper, the fly ash after denitrification (FAD) by SNCR method was used. CBPD is produced during clinker production in a rotary kiln, which is the most energy-intensive cement production process - for 1 ton of clinker is produced 0.6-1 tons of CO_2 [16, 18].

The aim of this paper is the application and testing of coatings on samples prepared from secondary raw materials. These samples are expected to be used to determine the coating adhesion and the resistance to scaling resistance on a sample with a specific coating and composition. Other expected outputs are moisture content tests, as well as compressive, flexural and tensile strengths.

2 Materials and Methods

For the experiment, secondary raw materials were used, namely finely grounded blast furnace slag (BFS) (Kotouč Štramberk Plc.) with a specific surface area of 400 m^2/kg and a specific weight of 2860 kg/m^3. Silica fly ash after denitrification (FAD) from the Ostrava-Třebovice power plant with a specific surface area of 500 m^2/kg and a specific weight of 2240 kg/m^3. Additionally, cement by-pass dust (CBPD) from the cement plant CAMMAC Plc. Horné Srnie with a specific weight of 2610 kg/m^3 was used. The use of this material in conventional concretes is problematic due to its high content of alkalies, chlorides, sulfates and free lime. These secondary raw materials were activated using anhydrous disodium metasilicate (Na_2SiO_3) (ADM) provided by Penta Chemicals. The aggregate used in this mixture was sand of 0/4 mm fraction from Tovačov.

The mixture used in this experiment has already been extensively tested and published in previous research [19, 20]. This mixture was selected because performing comparable or better results than the other tested hybrid alkali-activated mixtures. Another major advantage over the other mixtures is that this mixture uses the least amount of activator, which is positive in terms of the overall cost of the mixture being prepared. For this paper, this mixture was used again, with only one modification - compared to previous research, ordinary sand fraction 0/4 mm was used (standard quartz sand of 0/2 mm fraction was used in previous research). The main binder component in this mixture is therefore BFS, which accounts for 70% of the total binder component. The admixtures FAD and CBPD are equally 15% of the binder component. The composition of the mixture for the preparation of one standard form for 3 prisms (40x40x160) mm is given in Table 1.

Table 1. Mixture components for the preparation of a one standard form 3x (40x40x160).

Materials	BFS	FAD	CBPD	ADM	W	Sand
REC 3 [g]	315	67.5	67.5	62.30	215	1350

For the experiment, 40x40x160 mm prisms as well as 300x300x40 mm tiles were prepared. The preparation of the tiles was done in plastic forms which were greased with coconut emulsion. The surface of these products simulates the surface of concrete structures made of system formwork (smooth surface). For example, in producing concrete elements by the vibro-pressing compaction process, the surface of the concrete product is rougher due to the designed mix and production method. The prepared specimens were divided into two series namely, the sample that was wrapped in foil after demolding and the part of the samples that was stored in water (labelled "W"). The surfaces of the test bodies were prepared in two ways: the prisms and part of the tiles were roughened with a steel brush and the remaining tiles were roughened with a diamond grinding wheel. The samples prepared by brushing are hereafter referred to as 'B', while the samples roughened by the diamond wheel are referred to as 'R'. Subsequently, all samples were cleaned of dust using compressed air and then vacuumed.

Before the application of the coating, the moisture content of the materials was determined according to ISO 12 570 [21] by gravimetrically on selected prisms - the formula for calculating the moisture content is given in Equation 1, where “m” means weight of the sample before drying [kg] and m_0 means the weight of the dried sample [kg]. For the remaining samples, the moisture content was verified using a material moisture meter GMK 100 (Greisinger electronic, Senseca Germany GmbH, Germany) [21].

$$u = (m-m_0)/m_{0\ [hm.\%]} \tag{1}$$

Before applying the coating, the samples were left in a laboratory environment to dry to a stable weight. The coatings were carried out according to the requirements specified by the producers. The first coating served as a primer and the second coating was the final coating. Application of coating was by roller. Two types of coatings were used in the experiment, namely, two-component water-soluble epoxy coating (E) (MC-Bauchemie) and synthetic coating (S) (Datecha). The dry film thickness was determined according to EN ISO 2808 method 10 [22], namely with an ultrasonic thickness gauge - PosiTector 200 (Berg Engineering & Sales, Company, Inc., Rolling Meadows, IL, USA). The reference tensile strength of the tested material was determined by the R-formula according to EN 1542 [23] using the Proceq DY-216 (Screening Eagle Technologies AG, Switzerland). Coating adhesion to the surface was performed according to the same procedure on both surface modifications (R, B).

For the determination of the reference strengths, the samples were placed in a stable climate humidity chamber with a temperature of 20 ± 2°C and a relative humidity of 98% until the next testing. Compressive and flexural strengths were determined using a Form+Test MEGA 100-300-10 DM1 hydraulic press with Proteus software. The strengths were determined according to the EN 196-1 standard. The determination of flexural strength was performed by uniform loading at speeds of (50 ± 10) N/s. Compressive strength was determined by uniform loading at speeds (2400 ± 200) N/s [24].

The determination of resistance to the action of defrosting chemicals (scaling resistance) was also performed on elements measuring 40 × 40 × 160 mm according to the concrete standard ČSN 731326 in a freezer with automatic cycling. The test was performed according to method A of the relevant standard. The cycling temperatures were -15°C for 15 minutes and + 20°C again for 15 minutes. The specimens are placed into the freezer in the appropriate dishes into which the 3% sodium chloride solution is poured so that the specimen is immersed 5±1mm. After every 25 cycles, the loosened parts are drained off the dishes, dried at 105°C, and the mass waste is weighed [25].

3 Results

For purposes of this article, only the 28-day compressive and flexural strengths because the mixture had been investigated in previous studies. The compressive strength was around 68 MPa and the flexural strength was around 6.5 MPa. These results are slightly lower than when using standard quartz sand, where the results were published in [19], but the differences were only within standard deviations.

According to the producer's guidelines, the synthetic coating (S) can be applied only to surfaces with a moisture content lower than 15% - the moisture content of the samples had been determined before sample preparation and coating application. There is no strictly defined maximum moisture content for the two-component epoxy coating (E), but the coating must not be applied to a surface with distinct moisture maps. Moisture content has been determined by two methods, namely gravimetrically and using a material moisture meter. The gravimetrically verified moisture content of samples has been determined to be 7.2% for REC 3 samples and 7.4% for REC 3 W samples. The second method (material moisture meter) stated a moisture content of about 6.7% for both storage methods. This test verified that the coating could be applied to the prepared samples.

The dry film thickness determination results using the ultrasonic thickness gauge are shown in Table 2. Data with thickness are available on an open repository [26].

Table 2. Dry film thickness determined by ultrasonic thickness gauge (B - brushed with steel brush; R - roughened by diamond wheel; E - epoxy coating; S - synthetic coating) [26].

	REC 3				**REC 3 W**			
Surface preparation	B		R		B		R	
Coating type	E	S	E	S	E	S	E	S
Thickness [µm]	112.7	173.6	136.5	194.7	113.1	171.8	119.5	187.8
Standard deviation	7.5	8.8	6.5	5.2	8.3	8.7	7.9	3.2

The results show that the dry film thickness after two layers of coating is greater for the synthetic coating in all the tested samples. From the determination of the dry film thickness, coating thickness is greater for the samples that have been more roughened, which is because with a rougher surface, a slightly greater amount of paint needs to be applied to fully seal the surface with the coating and therefore the resulting dry film thickness is then slightly higher than with a smoother surface.

The test samples were also examined for tensile strength and coating adhesiveness. The results of these tests are shown in Figure 1. Data with tensile strength are available on an open repository [26].

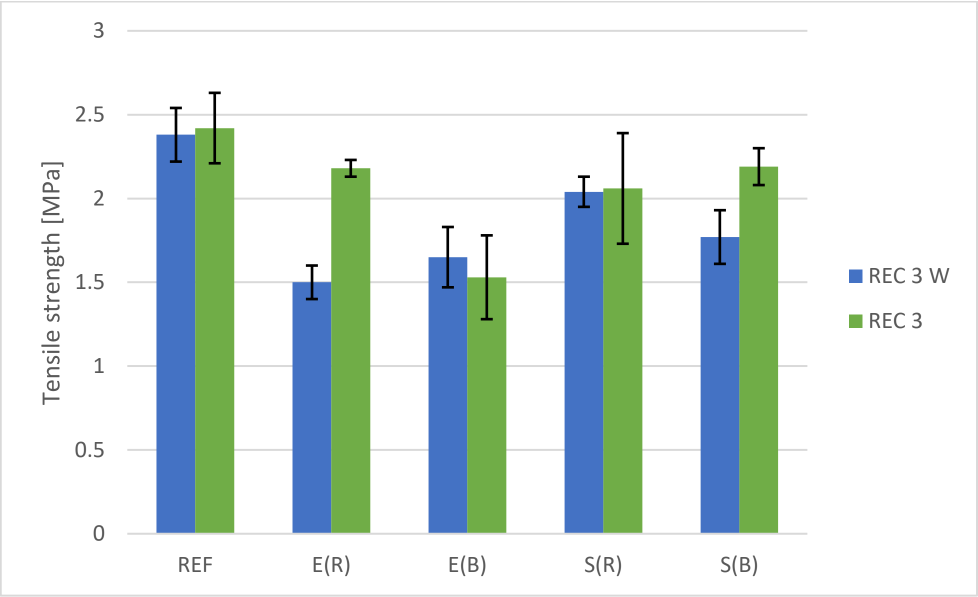

Fig. 1. Tensile strength and cohesion of coating test results [26].

The producer of the synthetic coating specifies a minimum tensile strength of the material for coating application as 1.5 MPa, which the tested mixture fulfils for both REC 3 and REC 3 W, as the tensile strength of this mixture is about 2.4 MPa. The adhesion of the synthetic coating (S) with the REC 3 surface ranged from 2.1 to 2.2 MPa for both surface treatments (B, R), while for the REC 3 W samples, the adhesion ranged from 1.8 to 2.0 MPa. The cohesion of the epoxy coating (E) with the surface was in the range of 1.5-1.7 MPa, except for the REC 3-E(R) sample, the adhesion of the coating with the surface was 2.2 MPa.

In terms of failure mode cohesive failure predominated over adhesive failure in the pull-off test. In only two cases did adhesive failure predominate over cohesive failure and this was in specimens that had been brushed (steel brush) and coated with an epoxy coating.

Furthermore, the samples for scaling resistance were tested. The REC 3 samples were cycled up to 100 cycles, while the REC 3 W samples were ended after 75 cycles due to high mass loss. The results of scaling resistance are shown in Figure 2. Data are available on an open repository [26].

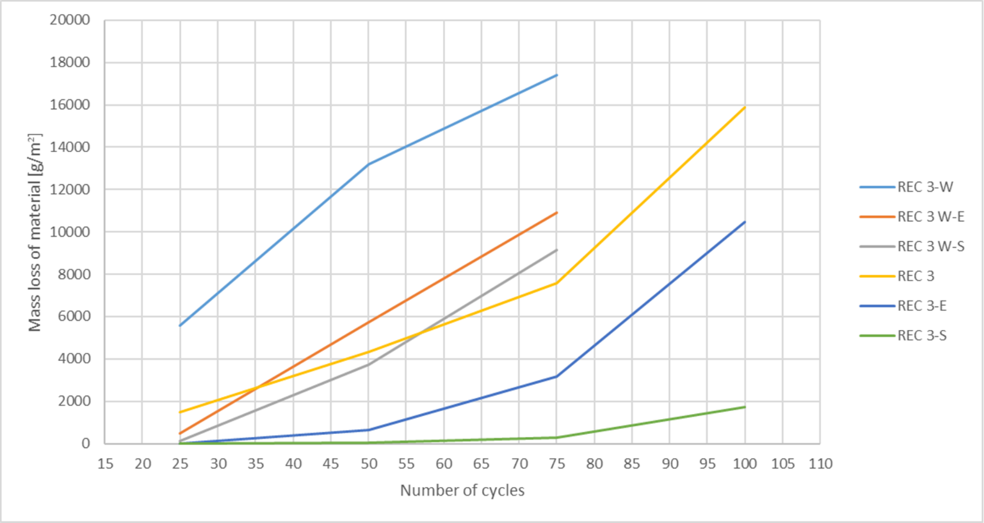

Fig. 2. Results of scaling resistance [26].

Although this test showed a positive effect of the coating on mass loss, the material is still unsuitable for use in such an environment where the product would be exposed to scaling resistance. Only REC 3-S showed a more significant positive effect on mass loss, with a total mass loss of 1710 g/m^2 after 100 cycles. B the results obtained, it can be concluded that the samples stored in the film (REC 3) are characterised by better scaling resistance.

In terms of frost resistance, the material shows good resistance to cyclic frost and thawing, as found in [20]. The freeze-thaw resistance of alkali-activated materials based on granulated blast furnace slag is mainly dependent on the amount and type of activator as shown in [27].

4 Discussion

Elnaggar et al. in their 2019 paper investigated the effect of asphalt-polyurethane coating on the durability properties of Portland cement-based concrete. The authors found that as the molar ratio (NCO/OH) increases, the dry film thickness increases, which the authors attributed to the higher density of the prepared coating. Also, the adhesion of the coating to the concrete surface increased with increasing molar ratio (NCO/OH), which is due to the increase in polar urethane bond, which has a positive effect on the adhesion properties [28]. Furthermore, the authors monitored the durability properties of the coated concrete when the samples were exposed for 28 days to 3% sulfuric acid, it was found that the compressive strengths decreased progressively with the length of exposure, with the lowest decreases again being achieved for the coating with the highest molar ratio (NCO/OH) [28].

In comparison, Almusallam, et al. in their 2003 work investigated the effect of different types of coatings from two different producers on the physical and durability properties of concrete. The following coatings were studied in the experiment: epoxy, acrylic, polyurethane, polymer emulsion, and chlor-rubber. The results were dependent on both the type of coating used and the producer of the coating. For example, for the absorption rate, different results were observed for the different coating producers. The greatest difference was achieved for the polyurethane coating, with one producer showing an absorption rate of 3.4 g/m^2/h and the other 36.6 g/m^2/h. On the other hand, for the polymer emulsion, there were only minimal differences between the producers, namely 55.6 and 59.7 g/m^2/h [29], respectively. In terms of chloride ion diffusion coefficient, the polyurethane coating from both producers was the most effective. The worst results were obtained for the polymer emulsion and the chlorinated rubber coatings [29].

5 Conclusion

The final dry film thickness is dependent on the roughness of the surface, with rougher surfaces resulting in a greater dry film thickness. The tested material with a surface layer tensile strength of around 2,4 MPa fulfils the condition of a minimum surface layer tensile strength of 1,5 MPa. The minimum cohesive strength of the coating with the surface was achieved for the epoxy coating and was around 1.5 MPa. Although this type of material showed a positive effect of the coating on the resistance of the material to the scaling resistance. The wastes are still orders of magnitude higher to fulfil the conditions and to be exposed to these environments.

Based on the type of failure in the pull-off test can be concluded that the adhesive properties of the coating exceed the tensile strength (cohesion) of the material itself.

Considering the existing research and results, the authors will focus on expanding the experimental program to include mixtures involving hybrid binder systems and hybrid concretes, where overall this can contribute to finding sustainable construction and building materials.

This paper was created as part of the project No. CZ.02.01.01/00/22_008/0004631 Materials and technologies for sustainable development within the Jan Amos Komensky Operational Program financed by the European Union and from the state budget of the Czech Republic.

References

1. Z. Liu, Z.Deng, S.J. Davis,C. Giron, & P. Ciais. Reviews Earth & Environment, **3**(4), 217–219. (2022)
2. O.E. Ige, O.A. Olanrewaju, K.J. Duffy, & C. Obiora, C. Journal of Cleaner Production, **324**, 129213 (2021)
3. T.A. Napp, A. Gambhir, T.P. Hills, N. Florin, & P.S. Fennell. Renewable and Sustainable Energy Reviews, **30**, 616–640 (2014*)*
4. E. Gartner. Cement and Concrete Research, **34**(9), 1489–1498 (2004)
5. C.A. Hendriks, E. Worrell, L. Price, N. Martin, L. Ozawa Meida, D. de Jager, & P. Riemer. Greenhouse Gas Control Technologies **4**, 939–944 (1999)
6. T. Luukkonen, Z. Abdollahnejad, J. Yliniemi, P. Kinnunen, & M. Illikainen. Cement and Concrete Research, **103**, 21–34 (2018)
7. CEMBUREAU. *Building carbon neutrality in Europe; Engaging for concrete solutions.*
8. B.C. Mendes, L.G. Pedroti, C.M.F. Vieira, M. Marvila, A.R.G. Azevedo, J.M. Franco de Carvalho, & J.C.L. Ribeiro. Journal of Building Engineering, **35**, 102010 (2021)
9. M.C.G. Juenger, F. Winnefeld, J.L. Provis, & J.H. Ideker. Cement and Concrete Research, **41**(12), 1232–1243 (2011)
10. A. Palomo, M.W. Grutzeck, & M.T. Blanco. Cement and Concrete Research, **29**(8), 1323–1329 (1999)
11. L. Deng, F. Yun, R. Jia, H. Li, X. Jia, Y. Shi, & X. Zhang. Materials Chemistry and Physics, **239**, 122039 (2020)
12. H. Wang, B. Ding, X. Zhu, Y. Tan, X.-Y. He & Q. Liao. International Journal of Heat and Mass Transfer, **113**, 286–294 (2017)
13. M. Sajid, C. Bai, M. Aamir, Z. You, Z. Yan & X. Lv. ISIJ International, **59**(7), 1153–1166 (2019)

14. Z. Giergiczny. Cement and Concrete Research, **124**, 105826 (2019)
15. Michalik, J. Babińska, F. Chyliński & A. Piekarczuk. Buildings, **9**(11), 225 (2019)
16. K. Wojtacha-Rychter, M. Król, M. Gołaszewska, J. Całus-Moszko, M. Magdziarczyk, & A. Smoliński. Journal of Building Engineering, **51**, 104309 (2022*)*
17. M. Oge, D. Ozkan, M. B. Celik, M. Sabri Gok & A. Cahit Karaoglanli. Materials Today: Proceedings, **11**, 516–525 (2019)
18. N.T. Abdel-Ghani, H. A. El-Sayed & A. A. El-Habak. HBRC Journal, **14**(3), 408–414 (2018)
19. L. Procházka, J. Boháčová & B. Vojvodíková. Materials, **15**(6), 2010 (2022)
20. L. Procházka, B. Vojvodíková & J. Boháčová. Crystals, **11**(9), 1033 (2021)
21. ČSN EN ISO 12570 Hydrothermal performance of building materials and products - Determination of moisture content by drying at elevated temperature; Office for Technical Standardization, Metrology and State Testing (2001)
22. EN ISO 2808 Paints and varnishes – Determination of film thickness; Office for Technical Standardization, Metrology and State Testing: Prague, Czech Republic (2020)
23. EN 1542 Products and systems for the protection and repair of concrete structures - Test methods - Measurement of bond strength by pull-off; Office for Technical Standardization, Metrology and State Testing: Prague, Czech Republic (2000)
24. EN 196-1 Methods of Testing Cement—Part 1: Determination of Strength; Office for Technical Standardization, Metrology and State Testing: Prague, Czech Republic (2005)
25. ČSN 73 1326 Determination of the Resistance of the Surface of Cement Concrete to the Action of Water and Scaling Resistance; Office for Technical Standardization, Metrology and State Testing: Prague, Czech Republic (1985)
26. Open repository on ZENODO. https://doi.org/10.5281/zenodo.10824490
27. V. Bilek, O. Sucharda & D. Bujdos. Sustainability, **13**(2), 473 (2021)
28. E. M. Elnaggar, T. M. Elsokkary, M. A. Shohide, B. A. El-Sabbagh & H. A. Abdel-Gawwad. Construction and Building Materials, **220**, 245–252 (2019)
29. A. A. Almusallam, F. M. Khan, S. U. Dulaijan & O. S. B. Al-Amoudi. Cement and Concrete Composites, **25**(4–5), 473–481 (2003)