

Article

# Attempts to Improve the Subsurface Properties of Horizontally-Formed Cementitious Composites Using Tin(II) Fluoride Nanoparticles

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Abstract: This article presents studies that were performed in order to improve the subsurface properties of horizontally-formed cementitious composites using tin(II) fluoride nanoparticles. The main aim of the study was to solve the problem of the decrease in subsurface properties caused by mortar bleeding and the segregation of the aggregate along the height of the overlay. The article also aims to highlight the patch grabbing difficulties that occur during the process of forming horizontally-formed cementitious composites. Four specimens were analyzed: one reference sample and three samples modified with the addition of 0.5, 1.0, and 1.5% of tin(II) fluoride nanoparticles in relation to the cement mass. To analyze the mechanical properties of the specimens, non-destructive (ultrasonic pulse velocity) and destructive tests (flexural tensile strength, compressive strength, abrasion resistance, pull-off strength) were performed. It was indicated that due to the addition of the tin(II) fluoride, it was possible to enhance the subsurface tensile strength and abrasion resistance of the tested cementitious composites. To confirm the obtained macroscopic results, the porosity of the subsurface was measured using SEM. It was also shown that the addition of the tin(II) fluoride nanoparticles did not reduce its flexural and compressive strength. The results show that horizontally-formed cementitious composites with the addition of 1.0% of tin(II) fluoride nanoparticles in relation to the cement mass obtained the most effective mechanical performance, especially with regard to subsurface properties.

Keywords: cement mortar; floor; overlay; tin(II) fluoride; nanoparticles; subsurface properties

# 1. Introduction

A necessary part of a building is the floor. The construction of the floor depends on the type of building. As a floor finish in industrial and public buildings, cementitious composites or epoxy resin coatings are commonly formed on concrete substrates. It was pointed out in [1] that epoxy resin coatings have a high mechanical and chemical resistance. However, due to their high price, cementitious composites (mainly cement mortar floors) are more often used as a floor finish. The process of forming cementitious composites has not been fully investigated and is still a very complex task.

For a cementitious overlay as part of a floor, the following properties are required: easy to install, durable, lightweight, flexible, slip- and dent-resistant, scratch- and abrasion-resistant [2]. Moreover, the overlay should be self-leveling for its preparation to be improved, and also have the lowest possible water-cement ratio in order to not have its mechanical properties decreased. Due to this, its



chemical composition must be properly prepared in order to obtain a desirable durability. In some cases, however, the cementitious overlay composition needs to be half-dry during floor finishing in order to keep it in an intact form after preparation involving manual patch grabbing (Step 4 in Figure 1). Moreover, depending on the functional requirements of an object as well as the durability of the overlay, they should have proper strength and functional parameters. The main strength and functional parameters are shown in Table 1.



Figure 1. Typical forming processes of horizontally-formed cementitious composites.

**Table 1.** The list of the main strength and functional parameters required from overlays made of cementitious composites.

Parameter	Value		
Compressive strength	Minimum 20 MPa		
Flexural strength	Minimum 5 MPa		
Subsurface tensile strength	Minimum 1.5 MPa		
Abrasion resistance	Maximum 22 cm <sup>3</sup>		
Hardness	Determined individually		

The important property of the cementitious overlays studied in [3] is their adhesion to the concrete substrate. A low adhesion strength value between the overlay and substrate can be responsible for the destruction of the floor structure. Thus, it is very important to correctly treat the concrete substrate surface before laying the overlay. The standard process recommends mechanical treatment of the concrete substrate surface with the use of sandblasting or grinding. Then, the substrate surface needs to be cleaned and treated with a bonding agent. Finally, the cement mortar overlay can be laid on this surface. The authors in [4] presented a potential use of texturing the concrete substrate instead of applying a bonding agent, before laying the cement mortar overlay. The research showed that it is possible to use the proposed method. For some methods, a higher adhesion strength result was obtained.

The process of forming horizontally-formed cementitious composites is as follows. First, on the concrete substrate, damp insulation is laid. Then, a layer of expanded polystyrene with additional damp insulation is added. Finally, the cement mortar overlay is applied (Figure 1). After curing of the overlay, and according to the owner's requirements, the finishing floor layer can be executed with wood parquet or ceramic tiles.

The destruction of horizontally-formed cementitious composites (e.g., overlays) also occurs in the subsurface area, where the strength properties of the cementitious material are lower. This problem

paste to be formed on the top surface of the overlay. The cement paste layer is known as laitance. The thin cementitious overlays are formed horizontally, and therefore, due to their large top surface area, there is a high risk of laitance occurring on this surface. This could dramatically decrease the strength of the overlay in its subsurface area. Hola et al. [5] presented a study of a floor with numerous defects. The velocity of the longitudinal ultrasonic wave  $c_{\rm L}$  results presented in this study show that an incorrectly prepared cement mortar mix and the incorrect supervision of the flooring process increase the possibility of laitance creation, thus causing a decrease in subsurface strength. Figure 2 presents the results of the compressive strength along the height of the floor, which were shown in the above-mentioned study. The microscale analysis is very helpful to understand the failure mechanism of the specimens [6]. Thus, Figure 2 includes a scheme that could help to understand the mechanism responsible for the decrease in strength. Water migration is responsible for the increase in the water-cement ratio in the subsurface area. After evaporation of the excess water in the subsurface area, more pores occurred. As a result, the strength properties of the subsurface area were lower in comparison to the deeper part of the overlay. Stawiski and Radzik [7], and Stawiski [8] also showed that the value of strength in the subsurface area of the overlay can sometimes differ significantly from the strength values in other parts of the overlay.



**Figure 2.** Scheme of the pore formation after mortar bleeding, with an illustration of the lowest compressive strength in the subsurface area (according to [5]).

As can be seen, for horizontally-formed cementitious composites, a significant reduction in strength for the subsurface zone was obtained. A layer of laitance and an increased porosity in this area is the reason for the reduction of the subsurface tensile strength  $f_h$ , abrasion resistance (greater volume loss,  $\Delta V$ ), hardness L, and subsurface compressive strength  $f_{cm}$ . Horizontal forming of the cementitious matrix does not significantly affect the flexural tensile strength  $f_{ct}$  and compressive strength  $f_{cm}$  of a full-size composite.

Moreover, the lower strength in the subsurface area could be the result of the segregation of the aggregate in a freshly laid material. Bui et al. [9] investigated this problem using the rapid testing

method. Rols et al. [10] studied the segregation resistance of self-leveling concrete. The properties of the samples were changed using different viscosity agents: starch, precipitated silica, and a type of waste from the starch industry. The obtained results show that starch and precipitated silica can enhance segregation resistance.

The addition of nanoparticles to cement-based composites is a new trend due to their increasing availability on the market and knowledge concerning their manufacturing [11–13]. The authors in [14] performed studies on overlays with the addition of amorphous silica nanospheres. Some properties such as subsurface tensile strength were improved, but abrasion resistance was worse when compared to the reference sample.

The main problems that occur during the process of forming cement-based overlays concern the patch grabbing process and the uneven segregation of the aggregate along the height of the material. Cementitious composites are horizontally-formed by manual or mechanical patch grabbing, and it is therefore hard to obtain high properties in the subsurface area. The compressive strength and flexural tensile strength of the overlays are generally satisfying, but in the subsurface area, the properties are lower. As a result, further processes such as the application of a finishing layer of the floor (wood parquet or ceramic tiles) are not possible because of cracks that occur in the subsurface area. This is why actions should be taken to find new additions to solve the above problems. Tin(II) fluoride (SnF<sub>2</sub>) nanoparticles can be seen as a material that has not been used previously to enhance the properties of horizontally-formed cementitious composites. Fluorine is mostly used as an addition to toothpastes. Some studies about teeth erosion and toothpaste with the addition of tin(II) fluoride were performed in [15], however, there is a lack of studies performed on cement mortar overlays.

In the last century, Allred and Rochow [16] proposed a simple approach based on electrostatic force to calculate electronegativity. The force of attrition between the nucleus and an electron from a bonded atom was described in Equation (1). In this study, *r* is the distance between an electron and a nucleus; *e* is the charge on the electron; and  $eZ_{eff}$  is the charge that is effective at the electron due to the nucleus and its surrounding electrons.

$$F_a = \frac{e^2 Z_{eff}}{r^2} \tag{1}$$

The values of  $Z_{eff}$  and r are different for each atom. Thus, after conducting calculations according to Allred and Rochow, the value of the attrition force that was obtained by the oxygen is classified in the eighth position among the atoms listed in the publication. In turn, the attrition force determined for the fluorine is 22% higher when compared to the oxygen, which gives it the fourth highest electronegativity value among the presented atoms.

Considering the above, the main purpose of this article was to use tin(II) fluoride nanoparticles as an additive to horizontally-formed cementitious composites in order to improve some properties such as compaction. Due to a high value of fluorine attrition force, it is possible to achieve a better bond with other atoms, which would in turn allow the main problems occurring in cement floors to be solved. The aim was also to test the mechanical properties of the horizontally-formed cementitious composites in their subsurface area.

#### 2. Significance of the Research

There is a lack of research in the literature that focuses on analyzing the addition of tin(II) fluoride nanoparticles to cementitious composites. This material is mostly used in the chemical industry as a component of toothpastes. The addition of tin(II) fluoride allows the compact toothpaste structure to be maintained and has a beneficial effect on enamel during its care. This phenomenon occurs because of the high electronegativity of F elements. This property is desirable for horizontally-formed cementitious composites. Therefore, the authors wished to propose a new approach by adding tin(II) fluoride nanoparticles to cement mortar overlay, while at the same time aiming to enhance the process of its formation and improve the properties of the obtained cementitious composite.

#### 3. Materials and Methods

The mortars were modified with the addition of  $SnF_2$  nanoparticles (Sigma Aldrich, Poznan, Poland). The cement mortars were used to form the overlays with a water–cement ratio of 0.30. The overlay was 40 mm thick and was laid on a substrate made of concrete class C30/37. The composition of each mortar per 1 m<sup>3</sup> of fresh matrix is given in Table 2, and information about the density of the components used to prepare the cementitious composites is presented in Table 3.

Series of Mortar		<b>R-0</b>	F-0.5	F-1.0	F-1.5
The content of SnF <sub>2</sub> nanoparticles	[%]	0.0	0.5	1.0	1.5
Tin(II) fluoride (SnF <sub>2</sub> ) Water Quartz sand Portland cement CEM I 42.5 R Superplasticizer Sika ViscoCrete 20 HE	[kg/m <sup>3</sup> ]	0.0 254 1155 847 4.3	4.2 254 1155 847 4.3	8.5 254 1155 847 4.3	12.7 254 1155 847 4.3

Table 2. Mix design of mortars.

Table 3. Bulk density and density of the components used to prepare the cementitious composites.

Component	Source	Bulk Density/Density		
Portland cement CEM I 42.5 R	Gorazdze Cement S.A. Heidelberg Cement Group, Gorazdze, Poland	1106 kg/m <sup>3</sup>		
Quartz sand	Mineral mine Margo, Mietkow, Poland	1497 kg/m <sup>3</sup>		
Superplasticizer Sika ViscoCrete 20 HE	Sika, Wroclaw, Poland	1080 kg/m <sup>3</sup>		
Tin(II) fluoride (SnF <sub>2</sub> )	Sigma Aldrich, Poznan, Poland	4.57 g/mL		

To the mixing water, 0.5% of the superplasticizer was added. The addition of nanoparticles to the mix took place during the mixing of the water and the superplasticizer with an automatic mixer. The mixing procedure started by slowly mixing the cement and water for 45 s (rotation speed: 8400 rph). Then, the cement paste with the addition of sand was slowly mixed for 45 s (rotation speed: 8400 rph). At the end, the fresh mix was mixed about two times faster than before for 18 s (rotation speed: 17,100 rph). The specimens were matured naturally in a relative air humidity of 60% ( $\pm$ 5%) and at an air temperature of +20 °C ( $\pm$ 3 °C).

Table 4 shows selected physical properties of the tin(II) fluoride SnF<sub>2</sub> nanoparticles (based on the supplier's data [17]). The chemical composition of the Portland cement CEM I 42.5 R is presented in Figure 3a. The grain curve of the washed quartz sand is shown in Figure 3b.

Table 4. Selected physical properties of the tin(II) fluoride (SnF<sub>2</sub>) nanoparticles (based on the supplier's data).

Nanoparticles	Property			
I	Molecular Mass [g/mol]	Melting Temperature [°C]	Boiling Point [°C]	Density at 25 °C [g/mL]
Tin(II) fluoride	156.71	215	850	4.57



**Figure 3.** Cementitious components information: (**a**) chemical composition of Portland cement CEM I 42.5 R (in mass %. based on supplier's data); (**b**) quartz sand grain curve.

Before applying the cement mortar on the concrete substrate, the consistency of the mix was determined using the Novikow cone (Figure 4a) in accordance with PN-B-04500 [18], the bulk density of the fresh mortar was determined in accordance with EN 1015–6 [19], and its setting time was designated using Vicat apparatus (Figure 4b) according to standard EN 196–1 [20]. After these tests, the cementitious overlay was horizontally-formed (laid) on the concrete substrate.



Figure 4. Measurements of (a) consistency using the Novikow cone; (b) setting time using Vicat apparatus.

Six specimens with dimensions of 40 mm  $\times$  40 mm  $\times$  160 mm were cemented from each mix and were used to perform the physical and strength property tests of the mortars in accordance with EN 13892–2 [21] (flexural tensile strength, Figure 5a; compressive strength, Figure 5b).







**Figure 5.** Performed destructive tests: (**a**) flexural tensile strength test; (**b**) compressive strength test; (**c**) abrasion resistance test; (**d**) subsurface tensile strength test.

Apart from executing the test elements, three specimens with dimensions of 71 mm × 71 mm × 71 mm were prepared from each mix. These were then used for the abrasion resistance test of the mortar in accordance with EN 13,892 [22] (Figure 5c). These specimens were stored together with the test elements in the same thermal and humid conditions until testing. The tests of the subsurface tensile strength  $f_h$  of the cement mortar were carried out using the pull-off method in accordance with EN 1542 [23] (Figure 5d), with the rebound number on the surface of the mortar being determined using the sclerometric method according to EN 12,504 [24].

Moreover, from each of the four samples, one core specimen with a diameter of 50 mm was taken from the mortar in order to perform tests of the velocity of the longitudinal ultrasound wave  $c_{\rm L}$  as a function of the thickness of the overlay using the ultrasonic method (Figure 6). Using a drill with a  $50 \pm 1$  mm diameter, core samples from the cementitious composites were obtained. On the lateral surfaces of the specimens, measuring points were applied at a spacing of 5 mm. For ultrasonic tests, special heads with a frequency of 40 kHz and a point contact with the tested surface were used [25]. The ultrasonic tests were carried out in order to determine how the ultrasonic longitudinal  $c_{\rm L}$  wave velocity changes along the direction of floor concreting. Each measurement of the longitudinal ultrasonic wave that was conducted in a selected measuring point was performed three times in order to obtain the values of the coefficient of variation below 5%.



**Figure 6.** Tests of the velocity of the longitudinal ultrasonic wave  $c_L$  as a function of the thickness of the overlay using the ultrasonic method: (a) scheme of the longitudinal ultrasonic wave test; (b) distribution of measuring points on the core specimen; (c) view of equipment; (d) view of the sample specimen during the ultrasonic tests.

In order to confirm the improvement of subsurface tensile strength, the results of the SEM tests on the samples with dimensions of  $11 \times 11 \times 11$  (mm) taken from the subsurface area of cement overlay

are presented. The samples were examined using a scanning electron microscope (SEM) in order to perform microstructural tests. This analysis was made using an SEM JEOL model JSM-6610A (Tokyo, Japan). The SEM was equipped with a tungsten hairpin filament and a backscattered electron (BSE) detector was used. The accelerating voltage of the BSE detector was equal to 20 kV, the beam current was equal to 40 nA, and the working distance was set to be equal to 10 mm. The samples for testing were first immersed in a non-conductive epoxy resin and then polished to an appropriate surface roughness of *Sa* = 310 nm (±35 nm). The surface roughness was controlled using the SEM Phenom G2 Pro with 5 kV acceleration and a resolution of 20 nm. A conductive path made of silver lacquer was then applied to the samples in order to obtain electrical conductivity and avoid electrical charging. The samples were then thermally sputtered in a vacuum of  $2 \times 10^{-5}$  Pa ( $2 \times 10^{-6}$  Torr) with graphite electrodes to obtain a conductive layer with a thickness of 20 nm.

#### 4. Results and Discussion

Figure 7 presents the results of the average setting times and the Novikow ( $I_N$ ) slump test as well as the bulk density of the fresh mortars for different contents of SnF<sub>2</sub> nanoparticles. All the tests were conducted three times, and the values of the coefficient of variation were below 5%.



**Figure 7.** Obtained results: (a) setting times and the Novikow ( $I_N$ ) slump test of the tested mortars; (b) the bulk density of the fresh mortar.

It can be seen from Figure 7a that the initial setting time accelerates for the samples with a higher amount of SnF<sub>2</sub> nanoparticles in the mortar. Sample F-1.5 started its initial setting time 70 min faster than the reference sample. With a higher addition of tin(II) fluoride in the cement mortar, the setting time was shorter. From a 0.0 to 1.5 percentage content of  $SnF_2$  nanoparticles in the cement mortar, in relation to the cement mass, the setting times were 105, 70, 70, and 50 min, respectively. The initial setting time of the prepared mortars started after 100, 90, 50, and 30 min, respectively. Sample F-1.5 obtained its final setting time after 80 min and resulted in being two times shorter than that obtained for the F-0.5 sample. The study in [26] observed that it was possible to reduce the setting time with the addition of nano-SiO<sub>2</sub> to concrete. The same relation was observed in [27], but this time in an alite-sulfoaluminate cement sample. Similar results of reduced setting time were obtained in [28], where nano-TiO<sub>2</sub> was added to the cement composites. The results presented by [29] showed that the setting time can also be delayed by adding 2CaO·SiO<sub>2</sub> nanoparticles to the concrete. The literature and the obtained results confirm that the nanoparticles have an impact on the setting time of concrete or cementitious composites. For the reference sample, the Novikow slump subsidence was 12 cm. The other cement mortars, with the addition of tin(II) fluoride, obtained an average result of Novikow slump subsidence of around 2 cm.

It is clear that the samples with a higher amount of  $SnF_2$  needed less time to obtain their initial and final setting time. This could be related to the higher electronegativity of the fluorine, which was added in the form of tin(II) fluoride to the fresh cement matrix. Quartz and calcium atoms (which occur in a high amount in the overlay) can interact better with fluorine atoms than oxygen atoms. Better compaction of these samples allowed the hydration process of the overlay to begin quickly, which improved the initial and final setting time. In the reference sample, the migration of water and the segregation of the aggregate could be the reason for the delayed initial and final setting time. The gentle movement of the water and aggregated particles significantly changes the results of setting times. Moreover, the influence of the addition of  $SnF_2$  on the higher compaction of the fresh cement matrix was confirmed by the Novikow slump subsidence test. The results showed that fluorine strongly affects other atoms by increasing the electrostatic force between them. As a result, it increased the compaction of the analyzed cementitious composite.

A faster initial and final setting time is desirable on site. During the laying and patch grabbing of fresh mortar, large areas of the building are not available for a specified period because of the curing time of the horizontally-formed cementitious composite. Thus, faster availability of the floor is desirable. The samples with the addition of tin(II) fluoride obtained this desirable property. The only negative result of a faster initial and final setting time is the lower possibility of correcting any mistakes that occur during the laying and patch grabbing of the fresh mortar.

Figure 7b presents the bulk density of each tested fresh cement mortar. The results show that the bulk density for the samples with the addition of  $SnF_2$  nanoparticles was higher. The bulk density for the reference sample and the sample with the addition of 0.5% of tin(II) fluoride nanoparticles was equal to 2260 and 2290 kg/m<sup>3</sup>, respectively. The last two samples (F-1.0 and F-1.5) obtained a similar result of around 2270 kg/m<sup>3</sup>.

The flexural tensile strength (Figure 8) of R-0 was 9.97 MPa  $\pm$  0.64 MPa. The results for the next three samples were similar, and the difference was around 2% (9.80 MPa  $\pm$  0.42; F-0.5), 7% (9.28 MPa  $\pm$  1.40; F-1.0) and 9% (9.09 MPa  $\pm$  1.46 MPa; F-1.5) in comparison to R-0. The compressive strength results presented in Figure 8 show that with a higher addition of SnF<sub>2</sub> nanoparticles, the  $f_{cm}$  value was still around 80 MPa. In comparison to the reference sample, which achieved 79.4 MPa ( $\pm$ 4.8 MPa; R-0), the lowest result was obtained for sample F-1.5, with a  $f_{cm}$  equal to 77.9 MPa ( $\pm$ 2.5 MPa). The compressive strength result of F-0.5 was 81.5 MPa ( $\pm$ 1.6 MPa), and for F-1.0, it was 81.0 MPa ( $\pm$ 1.3 MPa). It can be seen from Figure 8, in terms of the results for the compressive and flexural tensile strength, that the samples with tin(II) fluoride were very close to the reference sample. The standard deviation allows for the assumption that all the results are similar.



**Figure 8.** Test results of the mechanically compacted samples: (a) flexural tensile strength  $f_{ct}$ ; (b) compressive strength  $f_{cm}$ .

Studies performed in [30] show that with the addition of 1.5% of  $ZrO_2$ ,  $TiO_2$ ,  $Al_2O_3$ , or  $Fe_3O_4$  nanoparticles, the mechanical properties (compressive strength and flexural tensile strength) and the durability of concrete can be increased. The higher results of the compressive strength values obtained

for the cement-based materials were achieved with the addition of nano-SiO<sub>2</sub> [31] or nano-TiO<sub>2</sub> [32]. However, the results presented in Figure 8 show that the mechanical properties of cementitious composites did not change with the addition of  $SnF_2$  nanoparticles.

It can be seen from Figure 9a that the volume loss of the tested specimens decreases with the addition of  $SnF_2$  nanoparticles of more than 0.5%. The two first samples R-0 and F-0.5 lost 12.85 cm<sup>3</sup> (±0.88 cm<sup>3</sup>) and 12.63 cm<sup>3</sup> (±0.56 cm<sup>3</sup>) of their volume, respectively. The third (F-1.0) and fourth (F-1.5) samples lost significantly more of their volume than the other specimens (around 20% less than R-0 or F-0.5): 10.09 cm<sup>3</sup> (±0.46 cm<sup>3</sup>) and 10.63 cm<sup>3</sup> (±1.43 cm<sup>3</sup>), respectively. Figure 9b is correlated with Figure 7a and shows that the specimens lost from 22.0 to 27.6 g of their weight. It can be seen from Figure 9 that a higher compaction of the overlay, occurring due to the addition of tin(II) fluoride nanoparticles to the cementitious overlay, has a beneficial impact on its abrasion properties. It is assumed that the higher electronegativity of the fluorine will reduce the effect of mortar bleeding, which in turn will reduce the possibility of laitance formation on the top surface and thus increase abrasion resistance.



**Figure 9.** Results of testing the abrasiveness of cement mortars with regard to the content of  $SnF_2$  nanoparticles in relation to the cement mass: (**a**) volume loss  $\Delta V$ ; (**b**) weight loss  $\Delta m$ .

In the literature, it is hard to find research that is focused on the abrasion properties of cement-based materials with nanoparticle additives. Most of the research only mentions the studies performed in [33], where it was possible to enhance abrasion resistance properties by adding SiO<sub>2</sub> and TiO<sub>2</sub>.

Figure 10 presents the subsurface properties of the horizontally-formed cementitious floor layer. The subsurface tensile strength (Figure 10a) of the reference sample was 2.27 MPa (±0.42 MPa). The samples with the addition of tin(II) fluoride nanoparticles obtained higher  $f_h$  results: 2.80 MPa (±0.79 MPa; F-0.5), 3.05 MPa (±0.27 MPa; F-1.0), and 2.83 MPa (±0.32 MPa; F-1.5). The highest value of subsurface tensile strength with the lowest standard deviation was obtained by the sample with 1.0% of SnF<sub>2</sub>. It can be seen that with the addition of tin(II) fluoride nanoparticles, it is possible to increase  $f_h$  strength. Using the non-destructive method (Schmidt rebound hammer), the hardness of the samples was measured. The result of each test was the average of 12 rebound numbers. Therefore, the total number of rebound numbers was 48. The rebound number *L* for specimen R-0 (Figure 10b) was 53 (±7). The results of the other samples F-0.5, F-1.0, and F-1.5 were 50 (±2), 50 (±4), and 52 (±3), respectively. The obtained values were similar and between 50–53. However, a small decrease in subsurface tensile strength confirmed the better strength parameters of the subsurface area of the cementitious composite, which was probably obtained due to a low w–c ratio when compared to the reference sample.



**Figure 10.** Test results of (**a**) the subsurface tensile strength  $f_h$  of the cement mortar measured with the pull-off method; and (**b**) hardness assessed using the Schmidt rebound hammer method and described by the rebound number *L*.

Figure 11 shows the course of the longitudinal ultrasonic wave velocity  $c_L$  as a function of the thickness H of the tested cementitious overlays, which differed in terms of their content of  $SnF_2$  nanoparticles, in relation to the cement mass.



**Figure 11.** The course of the velocity of the longitudinal ultrasonic wave  $c_L$ : (**a**) as a function of thickness *H* of the overlay made of the tested mortars, which differed in terms of their content of SnF<sub>2</sub> nanoparticles in relation to the cement mass; (**b**) longitudinal ultrasonic pulse wave velocity in subsurface area (7 mm from the top of the surface).

It can be seen from Figure 11a that the reference sample's longitudinal ultrasonic wave speed at the top and in the middle of the sample (between 1.0 and 2.5 cm on the sample height) was around 1000–1200 m/s. The remaining cementitious overlays obtained much lower speed results of the longitudinal ultrasonic wave. The lowest value was 630 m/s. With a higher content of tin(II) fluoride in the cementitious overlay, the longitudinal ultrasonic wave speed was higher. Figure 11a shows that the sample with 1.0% of  $SnF_2$  nanoparticles obtained the most homogeneous structure across the sample height. The highest results of longitudinal ultrasonic wave speed were obtained by sample F-1.5, with results between 1015–1445 m/s. The specimens with the addition of tin(II) fluoride higher than 0.5% had much more uniform results of  $c_L$  than the other specimens. Such large differences in longitudinal ultrasonic wave velocity across the height of the tested cementitious overlays show that the addition of SnF<sub>2</sub> decreases the influence of mortar bleeding and aggregate segregation. The UPV tests also confirmed the suspicion of the fluorine electronegativity influence on the better compaction of the cementitious overlay along the specimen height. The ultrasonic pulse velocity test showed that the addition of tin(II) fluoride had a significant influence on the strength properties of the analyzed specimens.

Figure 11b shows the results of longitudinal ultrasonic wave velocity inside the specimens, 7 mm from the top of the surface. The subsurface tensile strength results presented previously (Figure 10a) were obtained from the area of the point where  $c_{\rm L}$  was measured (7 mm from the top surface). The obtained values correlate with each other, because the subsurface tensile strength and velocity of the longitudinal ultrasonic wave increased with the addition of SnF<sub>2</sub> for the samples with 1% of tin(II) fluoride. Therefore, the high strength properties for sample F-1.0 in its subsurface area, detected using the ultrasonic test, confirmed the high values of the subsurface tensile strength.

To confirm the high subsurface strength properties of the analyzed overlay, the authors decided to conduct the SEM test on  $11 \times 11 \times 11$  (mm) samples taken from the subsurface area of the cementitious specimens in order to analyze their porosity.

Figure 12 (from the left) shows the BSE images and grey scale histograms in the subsurface area for the reference sample (Figure 12a), the sample with the addition of 0.5% of SnF<sub>2</sub> (Figure 12b), the sample with the addition of 1.0% of SnF<sub>2</sub> (Figure 12c) as well as the one with the addition of 1.5% of SnF<sub>2</sub> (Figure 12d). In order to only analyze the cement matrix, the areas depicting the aggregate were cut out on the analyzed images.

From the greyscale histograms in Figure 12a, it can be seen that only the reference sample obtained a visible number of pores when compared to the samples with the addition of tin(II) fluoride. The results suggest that the reference sample probably obtains a higher number of pores, which was presumably due to mortar bleeding. The frequency of other elements: hydration products (HP) and calcium hydroxide (CH), seems to be similar for all of the specimens. The same applies to the peak of the non-hydratized cement grains (AH) that was observed on the histograms.

In the histograms shown in Figure 13, the threshold of greyscale, which defines the range of pores in the analyzed samples (red arrow), was determined. The determination of this greyscale threshold was carried out in accordance with the procedure defined in [34] in order to calculate the amount of segmented pores (on the right of Figure 13). For the analyzed images, the average fractional share of pores amounted to 18.54% for the subsurface area with the reference mortar (R-0), and 12.95% (F-0.5), 10.39% (F-1.0), and 9.43% (F-1.5) for the subsurface area of the mortar with the addition of SnF<sub>2</sub> nanoparticles. Thus, a decrease in the average fraction of pores in the subsurface area was visible and was reduced by almost twice for the samples with the addition of tin(II) fluoride when compared to the reference sample. The presented results corresponded with an increase in the subsurface tensile strength values. According to the authors, such a significant decrease in the level of adhesion. The SEM results also confirmed the influence of the high electronegativity of the fluorine on the increased compaction of the cement matrix and the reduction of mortar bleeding. This allowed a constant value of the previously designed water–cement ratio for the entire mix to be kept, and the possibility of laitance occurrence to be reduced.



**Figure 12.** Backscattered electron (BSE) image and greyscale histogram for the  $11 \times 11 \times 11$  (mm) samples taken from the subsurface area of the overlay of sample: (a) R-0; (b) F-0.5; (c) F-1.0; (d) F-1.5 (HP, hydration products, CH, calcium hydroxide, AH, non-hydratized cement grains).



**Figure 13.** Cumulative grayscale histograms and images of segmented pores (black pixels) for the samples: (**a**) R-0; (**b**) F-0.5; (**c**) F-1.0; (**d**) F-1.5.

### 5. Mechanical Performance Analysis of Overlay Mortars Modified with Tin(II) Fluoride

For the analysis of the mechanical performance of the overlays modified with tin(II) fluoride, the test results obtained in the research, which covered the basic mechanical properties of cement mortars (compressive strength  $f_{cm}$  and flexural tensile strength  $f_{ct}$ ), the subsurface tensile strength  $f_h$  of the cement mortars using the pull-off method, the abrasiveness of the cement mortars (volume loss

 $\Delta$ V), and the subsurface hardness assessed using the sclerometric method (described by the rebound number *L*) were used.

Based on the proposal given in [35], the mechanical performance ratio (MPR) was calculated. This ratio allows for the estimation of the mechanical performance of overlays modified with tin(II) fluoride nanoparticles in relation to the reference mortar. Depending on the type of building, a cementitious overlay can be used as a finish layer for the floor, or used as an underlay layer for wood parquet or ceramic tiles. The type of use defines the importance of each property of the overlay. Thus, the authors provided a mechanical performance analysis for two variants. The first variant was prepared for an overlay layer as a finish layer, and the second was prepared for an underlay layer. For each property, an individual weight was assigned in order to determine the mechanical performance ratio for the overlays modified with SnF<sub>2</sub> nanoparticles. For the first variant, the most important parameter was the abrasiveness of the cement mortars (volume loss  $\Delta V$ ), and its weight was assigned as 3. The weight of the second variant was assigned to the subsurface tensile strength  $f_{ct}$ , a weight of 1 was chosen. Therefore, the mechanical performance ratio for variant number one can be defined as:

$$MPR = \left(\frac{\left(3\cdot\left(\frac{\Delta V}{\Delta V_{(R-0)}}\right)\right) + \left(2\cdot\left(\frac{f_{h}}{f_{h(R-0)}}\right)\right) + \left(2\cdot\left(\frac{L}{L_{(R-0)}}\right)\right) + \left(1\cdot\left(\frac{f_{cm}}{f_{cm(R-0)}}\right)\right) + \left(1\cdot\left(\frac{f_{ct}}{f_{ct(R-0)}}\right)\right)}{9}\right)$$
(2)

For variant number two, the most important parameter characterizing the analyzed underlay layer was the subsurface tensile strength  $f_h$ , and its weight was assigned as 3. The other properties are less important. Therefore, weight 1 was assigned to the rest of the properties. The mechanical performance ratio for the second variant can be defined as:

$$MPR = \left(\frac{\left(3\cdot\left(\frac{f_h}{f_{h(R-0)}}\right)\right) + \left(1\cdot\left(\frac{\Delta V}{\Delta V_{(R-0)}}\right)\right) + \left(1\cdot\left(\frac{L}{L_{(R-0)}}\right)\right) + \left(1\cdot\left(\frac{f_{cm}}{f_{cm(R-0)}}\right)\right) + \left(1\cdot\left(\frac{f_{ct}}{f_{ct(R-0)}}\right)\right)}{7}\right)$$
(3)

Table 5 summarizes all the obtained results in relation to the reference overlay R-0 and the mechanical performance ratio calculated according to Equations (2) and (3). The absolute values for mortar R-0 are:  $f_{cm} = 79.4$  MPa,  $f_{ct} = 12.2$  MPa,  $f_h = 2.27$  MPa (shot-blasted surface),  $\Delta V = 12.85$  cm<sup>3</sup>, L = 53.

Series of Mortar	ΔV/ΔV <sub>(R-0)</sub> Abrasiveness	<i>f<sub>h</sub>/f<sub>h(R-0)</sub></i> Subsurface Tensile Strength	<i>L/L</i> <sub>(R-0)</sub> Hardness	<i>fcm/fcm</i> (R-0) Compressive Strength	<i>f<sub>ct</sub>/f<sub>ct(R-0)</sub></i> Flexural Strength	MPR (%) Mechanical Performance Ratio
			Variant No. 1			
R-0	$1.00 \times (3)$	$1.00 \times (2)$	$1.00 \times (2)$	$1.00 \times (1)$	$1.00 \times (1)$	100.0
F-0.5	$1.02 \times (3)$	$1.23 \times (2)$	$0.94 \times (2)$	$0.98 \times (1)$	$0.98 \times (1)$	104.1
F-1.0	$1.21 \times (3)$	$1.34 \times (2)$	$0.94 \times (2)$	$1.03 \times (1)$	$0.93 \times (1)$	113.1
F-1.5	$1.17 \times (3)$	$1.25 \times (2)$	$0.98 \times (2)$	$1.02 \times (1)$	$0.91 \times (1)$	110.1
			Variant No. 2			
R-0	$1.00 \times (1)$	$1.00 \times (3)$	$1.00 \times (1)$	$1.00 \times (1)$	$1.00 \times (1)$	100.0
F-0.5	$1.02 \times (1)$	$1.23 \times (3)$	$0.94 \times (1)$	$0.98 \times (1)$	$0.98 \times (1)$	108.9
F-1.0	$1.21 \times (1)$	$1.34 \times (3)$	$0.94 \times (1)$	$1.03 \times (1)$	$0.93 \times (1)$	116.4
F-1.5	$1.17 \times (1)$	$1.25 \times (3)$	$0.98 \times (1)$	$1.02 \times (1)$	$0.91 \times (1)$	111.8

**Table 5.** Results of the tested properties in relation to the reference overlay R-0 with Mechanical Performance Ratio (MPR).

It is visible from Table 5 that all of the samples with  $SnF_2$  obtained a higher MPR value in comparison to the reference overlay. It shows that the addition of tin(II) fluoride to the cement matrix improves the most important properties of the horizontally-formed cementitious composite. For variant numbers one and two, the highest mechanical performance ratio was obtained by sample F-1.0, with MPR results of 113.1% and 116.4%, respectively. Regardless of the type of use, the cementitious overlay with the addition of 1.0% of tin(II) fluoride turned out to be the best.

# 6. Conclusions

The purpose of this article was an attempt to evaluate the improvement of the subsurface properties of horizontally-formed cementitious composites modified with tin(II) fluoride nanoparticles. Based on the performed tests, the following conclusions can be drawn:

- Forming horizontally-formed composites is not an easy task. The subsurface strength properties of the overlay are weaker if the forming process is incorrectly done (the possibility of laitance occurrence is higher). Thus, with the addition of tin(II) fluoride nanoparticles, it is possible to not only compact the lower parts of the overlay, but also to more effectively compact the higher near-surface parts, which are much more important due to their protection properties in a floor structure. The addition of SnF<sub>2</sub> allows the forming process of horizontally-formed cementitious composites to be enhanced. The benefits of it are the more effective process of forming high-quality floors and the higher strength properties of the subsurface overlay area,
- The samples with the addition of SnF<sub>2</sub> had similar compressive strength results and slightly lower flexural tensile strength results than the reference sample. However, the standard deviation of flexural tensile strength allows for the assumption that the results are also similar to those obtained by the R-0 specimen. The UPV test results showed that the c<sub>L</sub> values were similar in the middle of all the samples, which is why there was no visible difference in the obtained strength results. The measured values were much higher than the minimal required strength values. The addition of tin(II) fluoride did not have a significant influence on f<sub>cm</sub> and f<sub>ct</sub>.
- By adding tin(II) fluoride, it was possible to increase the abrasive resistance of the tested elements. Sample F-1.0 lost 21% more of its weight than the reference sample. Then, the ultrasonic tests showed that sample F-1.0 obtained the highest results of the velocity of the longitudinal ultrasonic wave. Moreover, from the presented SEM test results, it can be seen that sample F-1.0 had 46% lower porosity in its subsurface area than the reference sample, which could have been obtained as a result of the high electronegativity of the fluorine additive. Its high attrition force with other atoms of the mortar matrix allowed a very compacted overlay structure to be obtained. It can be assumed that lower porosity means that the amount of water in the subsurface area was also lower. This had an impact on the lower water–cement ratio and higher strength properties, and contributed to the elimination of the laitance layer. Abrasive resistance is a very desirable property for tested structures because of its influence on the life cycle durability of the overlay.
- The addition of tin(II) fluoride has a visible impact on the subsurface strength properties of horizontally-formed cementitious composites. From the course of the velocity of the longitudinal ultrasonic wave, it can be seen that overlays with  $SnF_2$  obtained much higher velocity results in the top area than sample R-0. The mortar bleeding and aggregate segregation process was observed for the reference sample. This phenomenon was reduced for the samples with the addition of tin(II) fluoride, and the high electronegativity of fluorine could have a significant impact on it. The results of the Novikow slump subsidence test and analysis of the SEM images showed that this hypothesis is proper, which was confirmed by the mentioned tests. Thus, because of better adhesion caused by lower porosity, the subsurface tensile strength increased with a higher amount of  $SnF_2$ . The best result was obtained by sample F-1.0, with  $f_h$  being equal to 3.05 MPa (±0.27 MPa). However, the result obtained by F-1.5 was similar. Moreover, the results of the subsurface tensile strength corresponded with the velocity values that were measured in this area, which

is confirmed by the presented results. The Schmidt rebound hammer results showed that the subsurface hardness of the samples was similar.

- Due to the high results of the parameters that are required for cementitious overlays, the mechanical performance analysis showed that sample F-1.0 obtained the best MPR results (113.1% and 116.4%) for the two considered variants.
- The overlay should be formed in such a way that it has as smooth a top surface as possible when it is designed as a finishing layer. All of the roughness needs to be removed with mechanical treatment. Thus, the addition of tin(II) fluoride allowed the patch grabbing process to be improved, without obtaining any unintended inequalities on the overlay surface.

Summarizing the above, the higher electronegativity of the fluorine, when compared to oxygen, allowed the properties of the cementitious overlay, especially its subsurface properties, to be increased. This resulted in a better compaction of the matrix as well as the reduction of laitance and porosity. According to the obtained results, the authors would like to present the mechanism of the behavior of the fresh cementitious matrix with and without the addition of tin(II) fluoride, which is presented in Figure 14.



**Figure 14.** The observed influence of the interaction between the tin(II) fluoride atoms and the components of the fresh cementitious overlay on the improvement of the compaction of the matrix.

#### 7. Perspectives

It has been observed in the presented research that the addition of tin(II) fluoride ( $SnF_2$ ) has a positive impact on some subsurface strength properties (subsurface tensile strength, abrasion resistance) of horizontally-formed cementitious composites. The proposed addition of  $SnF_2$  can also enhance the process of forming cement-based overlays. However, future studies are needed in order to continue to develop this interesting and complex topic and phenomena. It is suggested that these studies may include:

• The analysis of different configurations of SnF<sub>2</sub> additions to cementitious composites;

- The study of the early-age properties of cementitious composites modified with the addition of SnF<sub>2</sub> (e.g., hydration);
- The study of the effect of SnF<sub>2</sub> on the corrosion resistance and/or other durability related phenomena of modified cement-based composites;
- The explanation of some of the chemical reactions that occurred (e.g., interaction between tin(II) fluoride and the rest of the ingredients of cementitious composites) with verification of the hypothetical chemical bonding between them at the nano-scale;
- The verification of the pull-off adhesion and bonding strength between an overlay modified with the addition of SnF<sub>2</sub> and differently prepared concrete substrates, and also support this with more advanced microstructural tests that use well established procedures (e.g., scanning electron microscopy, micro-computed tomography or nanoindentation).
- Analysis of the hydration process of the cementitious overlay with the addition of SnF<sub>2</sub>.

The authors would also like to highlight that the problem of the proposed solution is the high price of the nanoparticles. The use of the tin(II) fluoride will be economically rational if the price of  $SnF_2$  decreases. However, the presented results are promising and there is a definite need to continue them.

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