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Proceeding Paper

The Impact of Waste Fluid Catalytic Cracking Catalyst Addition on the Selected Properties of Cement Pastes †

Paweł Niewiadomski [1,*] and Michał Cisiński [2]

[1] Department of Materials Engineering and Construction Processes, Wroclaw University of Science and Technology, Wybrzeże Wyspiańskiego 27, 50-370 Wroclaw, Poland
[2] Department of Advanced Material Technologies, Wroclaw University of Science and Technology, Wybrzeże Wyspiańskiego 27, 50-370 Wroclaw, Poland
* Correspondence: pawel.niewiadomski@pwr.edu.pl; Tel.: +48-508-859-290
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Abstract: The significant reduction in CO_2 emissions arising from the cementitious composites industry is one of the highest priorities for the construction sector's movement towards climate neutrality and sustainable development. One of the approaches to cope with this issue is to partially substitute cement with supplementary cementitious materials. Recently, various oil refinery wastes (ORW) have attracted researchers' attention in terms of being investigated for such an application. As such, the present paper shows the preliminary results of investigations conducted on cement pastes with the addition of a spent fluid catalytic cracking catalyst derived from a Polish oil refinery company. It is worth mentioning that the incorporation of ORW in cementitious composites might enable the production of more environmentally friendly construction materials without sacrificing quality, whilst, simultaneously providing an opportunity for recycling petrochemical wastes.

Keywords: oil refinery wastes; spent FCC catalyst; cementitious composites; cement pastes; supplementary cementitious materials; sustainable development

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1. Introduction

1.1. Supplementary Cementitious Materials towards Construction Sustainability

Global urbanization and economic growth have increased society's demand for new buildings and infrastructure and hence for concrete, the scale of usage of which makes it currently the most commonly consumed material, after water, worldwide [1] (pp. 35–42). However, the production process of cement, with its crucial constituent used as a binder, is based on quarrying, and requires high temperatures and considerable energy consumption, contributing to natural resource depletion and significant CO_2 emission; it accounts for 5–8% of global emissions of this greenhouse gas [2] (pp. 169–174). Therefore, for the sake of natural environment, the construction sector is obligated to drastically reduce its CO_2 emissions to reach the goal of sustainable development whilst simultaneously filling the increasing market demand for cementitious composites. One of the approaches to cope with this issue is to partially substitute cement with supplementary cementitious materials (SCMs) with pozzolanic properties [3]. Despite the fact that a huge number of various waste materials and by-products derived from agricultural and industrial activities were investigated regarding such applicability, it is mainly fly ash, ground-granulated blast-furnace slag and silica fume that have already been implemented on industrial scale [4] (p. 3136).

1.2. Oil Refinery Waste Recycling

Recently, various waste materials derived from petrochemical industry, i.e., oil refinery wastes (ORW) have caught researchers' attention in terms of being investigated as a potential green resource for the construction sector. One considerable type of solid ORW is spent catalysts; they are generally used to promote the conversion processes of crude oil into petrochemical products. These materials become deactivated after a period of time being used in the refining processes, due to the mechanical degradation and most notably contamination with various pollutants from processing resources which, while adsorbed on their structure, reduce their specific surface area and thus their catalytic activity. Consequently, spent catalysts are withdrawn from petrochemical installations of single-complex oil refinery companies in an estimated annual amount of 5515 tonnes [5]. It should also be pointed out that almost 10% of that quantity is represented itself by spent catalysts withdrawn from fluidized catalytic cracking units, which makes them the largest group of catalytic wastes in the worldwide petrochemical industry [5]. Unfortunately, the majority of these waste materials are consequently sent to landfills, thereby providing economical losses for companies, and serious health risks related to the release of chemical pollutants into the natural environment [2] (pp. 169–174). Apart from organic compounds, spent FCC catalysts might also contain heavy metals, such Cr, Pb, and Ni [6] (pp. 111–118). Therefore, finding a newer, safer application for these waste materials is necessary. A reasonable research direction for this purpose seems to be the use of ORW as partial cement substitutes in cementitious composites. Such a procedure, apart from reducing cement usage, might potentially allow the binding of chemical pollutants in their hardened state to the composite structure, thereby minimizing the risk of their release to the environment [6] (pp. 111–118). Moreover, as waste recycling is the most preferable option for managing waste materials and moving towards a circular economy, the suitability of such direction is clearly underlined.

1.3. Recent State of the Art Knowledge

In the literature, spent FCC catalysts are predominantly investigated in ORW material, regarding their applicability in construction sector. Accordingly, the substitution of up to 25–30% of cement, by mass, with spent FCC catalysts derived from, e.g., Lithuanian [7] (pp. 103–108), Chinese [8] (pp. 1773–1783), Spanish [9] (pp. 12–17) Portuguese [10] (pp. 109–121) and Oman [11] (pp. 77–81) oil refineries contributed to the mechanical strength enhancement of hardened state cementitious composites. However, even though the incorporation of this waste material typically contributes to rheological properties' deterioration of cementitious composites mixes, which has been confirmed in many works such as [8–10], this negative effect might be reduced by using plasticizing admixtures. Nonetheless, it should be pointed out that the oil-refining catalysts are manufactured individually for each oil refinery company to obtain the most favorable properties, i.e., activity and selectivity, tailored to the specific conditions in the petrochemical installations and depending on many different factors such as type of processing crude oil resources and oil refinery complexity. Therefore, the specific properties, chemical composition and potential pollutants of spent FCC catalysts, as well as of other ORW, might be significantly variable between the oil refineries from which they are withdrawn. This might be considered a key limitation in terms of freely using these materials in construction practice. As such, an individual approach is required for assessing the feasibility of recycling ORW in cementitious composites [2] (pp. 169–174).

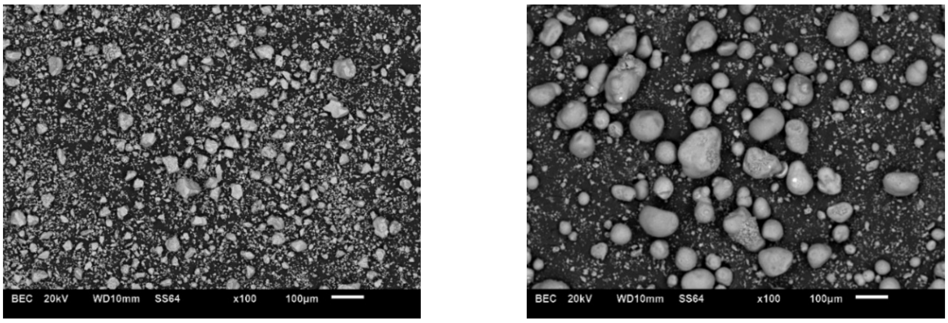
1.4. Aim of the Research

The aim of the conducted research was to assess the potential of spent FCC catalysts derived from a Polish oil refinery company, to be recycled as a partial cement substitute for the production of sustainable cementitious composites. As such, the work consists of preliminary research carried out on basic cementitious composites, i.e., cement pastes, with the addition of a spent FCC catalyst used as a partial cement substitute within the range of 0 to 20%, by mass. The cement pastes have been prepared with water to a binding (cement + spent catalyst) ratio of 0.3. The influence of spent catalysts on their selected properties was investigated through the measurements of slump flow, compressive strength, flexural strength, water absorptivity and microstructure. For the purpose of future investigations, we plan to expand the scope of the current research by investigating cement pastes prepared with different w/b ratios (e.g., 0.35, 0.40). Moreover, tests will also be conducted on cement mortars. Apart from spent FCC catalysts, we plan also to investigate a few other types of ORW.

2. Materials and Methods

2.1. Materials Characteristic

The spent FCC catalyst used in this research was supplied by a Polish oil refinery company. The role of FCC catalysts in the petrochemical industry is to promote the cracking reaction of high-boiling oil fractions into lower-boiling hydrocarbons for blending commercial fuels. From the physicochemical viewpoint, this waste material might be characterized as a white-grey powder. In the research, it was used as a substitute of cement (CEM I 52.5R). The microstructures of these materials have been presented in Figure 1 in the form of SEM images at ×100 magnification. Their chemical compositions, obtained using X-ray fluorescence spectrometer analysis (XRF) and from [12] for the spent catalyst and cement, respectively, have been presented in Table 1. Accordingly, the mean particle size of cement grains is finer than in case of the spent catalyst which, as a typical pozzolanic material, is mainly composed of SiO_2 and Al_2O_3.



(**a**) (**b**)

Figure 1. SEM images of microstructure of the materials: (**a**) cement; (**b**) spent FCC catalyst.

Table 1. Chemical composition of the materials, wt.%.

Material\Oxide	**SiO_2**	**Al_2O_3**	**CaO**	**Fe_2O_3**	**MgO**	**SO_3**	**Other**
Cement (CEM I 52.5R)	20.09	4.84	64.02	3.87	1.15	2.83	3.20
Spent FCC catalyst	44.48	38.11			3.43	3.88	10.10

2.2. Formulations of Cement Paste Mixes

The cement paste mixes were prepared by mixing of ingredients in the laboratory bowl. The spent FCC catalyst was used as a substitute of 0%, 5%, 10%, 15% and 20% of cement. The water to binder (w/b) ratio of 0.3 was kept constant for all of the formulations of mixes. Accordingly, the reference (plain cement) mix is described as 0.30 ref, while subsequent substituted mixes are described as 0.30 5%, 0.30 10%, 0.30 15% and 0.30 20%, corresponding to the cement substitution level with the spent catalyst, i.e., 5%, 10%, 15% and 20%, by mass, respectively. The complete formulations of paste mixes have been listed in Table 2.

Table 2. Formulations of 1 dm^3 of cement paste mixes.

Material\Mix (1 dm^3)	0.30 ref	0.30 5%	0.30 10%	0.30 15%	0.30 20%
Cement [kg]	1.593	1.508	1.423	1.340	1.257
Spent FCC catalyst [kg]	0.000	0.079	0.158	0.236	0.314
Substitution level [%]	0	5	10	15	20
Water [kg]	0.478	0.476	0.474	0.473	0.471

2.3. Evaluation of the Flowability of Cement Paste Mixes

The flowability of cement paste mixes was measured through the flow table test, according to the PN-EN 1015–3:2000. The truncated cone-shaped mold was placed on the spreader disc, and the cement paste mix was applied in two layers, thickening each for at least 10 strokes of the compactor. Then, the excess paste was scraped off, and after 15 s, the mold was slowly removed by lifting it vertically. After shaking the disc 15 times, two diameters of the mix oriented perpendicularly to each other were measured, and their average value was assumed to be the final one.

2.4. Evaluation of Mechanical Properties of Cement Paste Samples

The mechanical properties of the cement paste samples were determined through measurements of flexural and compressive strength. The tests were carried out on beam (40 × 40 × 160 mm) and cubic cement paste samples (40 × 40 × 40 mm), respectively, both at 7th and 28th curing day with the use of an electromagnetic universal testing machine with a load cell capacity of 300 kN.

2.5. Evaluation of Water Absorptivity of Cement Paste Samples

The water absorptivity of the cement paste samples was evaluated as follows: the mass 'A' of cement pastes was measured after removing all uncombined water through drying the samples to a constant weight. Subsequently, the samples were placed in the vessel with water. Immediately after the samples were removed from the vessel, their surfaces were carefully dried with a cloth. After that, the mass 'B', corresponding to the maximum saturated cement paste samples, was measured. The water absorptivity was calculated as the difference between B and A in relation to A, and is expressed in percentages.

2.6. Evaluation of Microstructure of Cement Paste Samples

The microstructure of the surface of the cement paste samples was observed using scanning electron microscopy (SEM JEOL model JSM-6610A) with secondary electron mode.

3. Results

3.1. Rheological Properties of Cement Paste Mixes

The results of slump flow values obtained for the respective cement paste mixes have been presented in Figure 2. It may be seen that the slump flow of the investigated mixes generally tends to decrease with the increase in cement substitution level. However, the 0.30 5% mix reveals the highest slump flow of all investigated mixes, i.e., 182.5 mm.

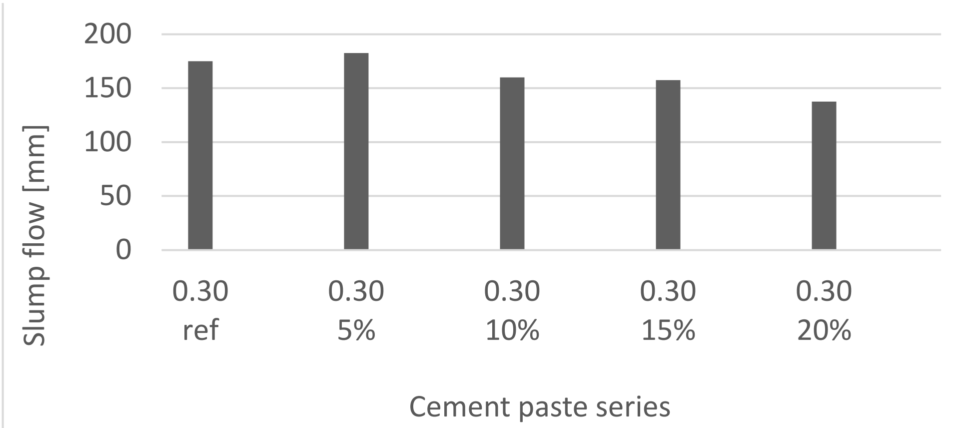


Figure 2. Effects of cement substitution with spent FCC catalyst on the slump flow of cement paste mixes.

3.2. Mechanical Properties of Cement Paste Samples

3.2.1. Compressive Strength

The results of 7- and 28-day compressive strength (CS) values obtained for the cement paste samples have been presented in Figure 3. Accordingly, the CS of each cement paste with the addition of the spent catalyst was found to be higher in comparison with the 0.30 ref sample, both at the 7th and 28th day of hydration. The highest 7- and 28-day CS values were measured for 0.30 15% and 0.30 10% sample, respectively, exceeding the CS of 0.30 ref for 36% and 17%, respectively. As expected, the CS enhances with the curing age.

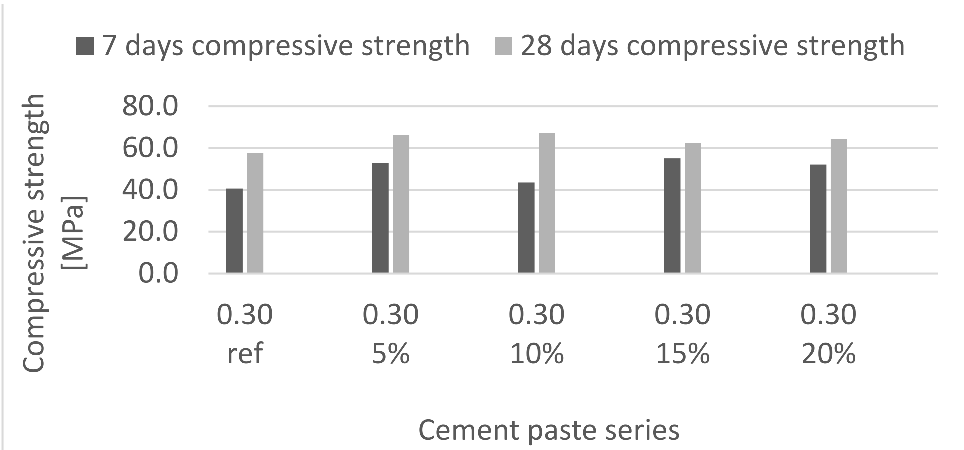


Figure 3. Effects of cement substitution with a spent FCC catalyst on the 7- and 28-day compressive strength of cement paste samples.

3.2.2. Flexural Strength

The results of 7- and 28-day flexural strength (FS) values obtained for the respective cement paste samples have been presented in Figure 4. Accordingly, the FS tends to decrease with the increase in cement substitution level, mentioning that the FS of the respective samples is generally similar between the 7th and 28th day of hydration.

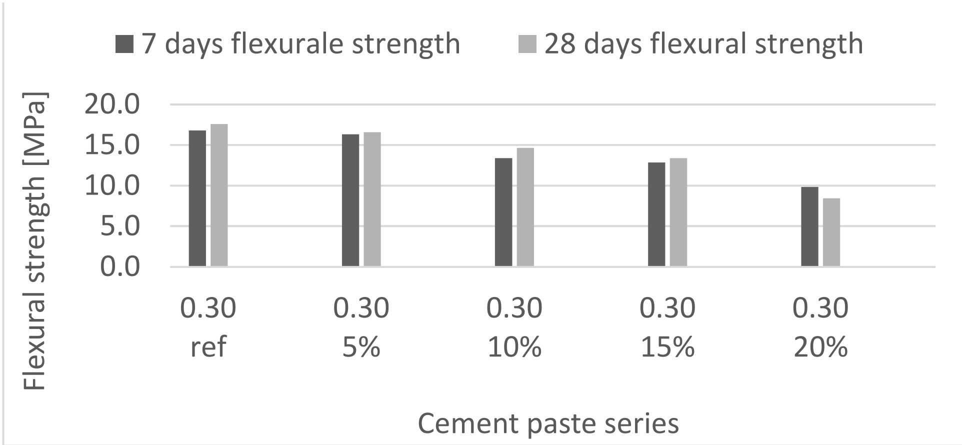


Figure 4. Effects of cement substitution with a spent FCC catalyst on the 7- and 28-day flexural strength of cement paste samples.

3.3. Water Absorptivity of Cement Paste Samples

The results of water absorptivity values obtained for the respective cement paste samples have been presented in Figure 5. Considering the results, it might be stated that the water absorptivity of 0.30 5% is similar to 0.30 ref. However, as 10% and more of cement is substituted with spent catalyst, the water absorptivity increases. The values obtained for 0.30 10%, 0.30 15% and 0.30 20% are also similar to each other, nonetheless, exceeding 0.30 ref for 17%, 14% and 17%, respectively.

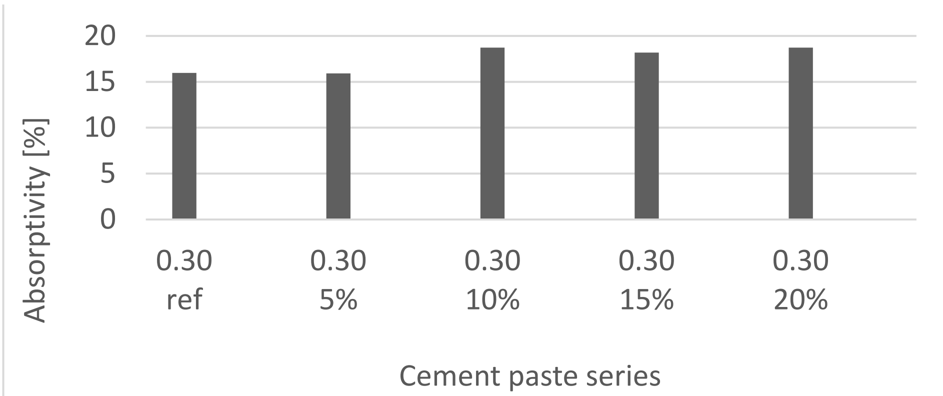
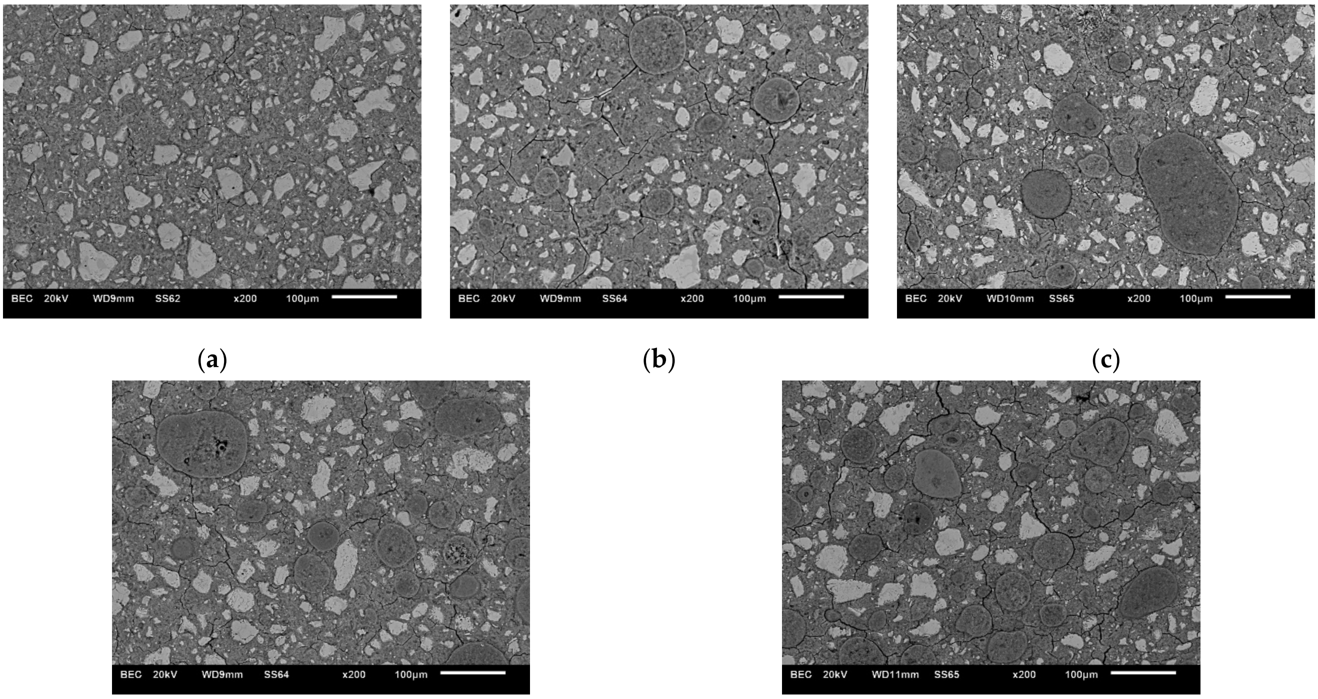


Figure 5. Effects of cement substitution with spent FCC catalyst on the water absorptivity of cement paste samples.

3.4. Microstructure of Cement Paste Samples

The microstructures of the cement paste samples have been presented in Figure 6 in the form of SEM images at ×200 magnification. On the basis of the greyscale of the images, the components and pores were identified. The light grey shapes correspond to the unhydrated cement grains, whilst the coarser spherical shapes in darker color are attributed to unreacted spent catalyst particles. Accordingly, the pores, which might be seen as a black pixels, are mainly identified in the interphase transition zone (ITZ) between spent catalyst and CSH gel. Therefore, their content was found to increase with the increasing cement substitution level. As such, the matrix of the 0.30 ref was found to the be more homogenous and uncracked when compared to those matrices of the samples with spent catalyst addition.



(**a**) (**b**) (**c**)

(**d**) (**e**)

Figure 6. SEM images of microstructure of the respective cement paste samples: (**a**) 0.30 ref; (**b**) 0.30 5%; (**c**) 0.30 10%; (**d**) 0.30 15%; (**e**) 0.30 20%.

4. Discussion

The negative effect of the addition of spent FCC catalysts on the slump flow and rheological properties of cement paste mixes was found to be in accordance with the literature results [8–10]. This finding might be generally attributed to the very high specific surface area of spent catalysts, which is provided by highly porous zeolite structure and identified in [8] (pp. 1773–1783). Thereby, spent FCC catalysts are a water-demanding material which contribute to the reduction of available water in the system and hence the workability of fresh mixes. The slump flow value of the 0.30 5% mix was found to be in the scope of standard deviation thresholds of 0.30 ref, and thus the slight increase in slump flow between those mixes was assumed to be the result of a measurement statistic.

The development of the compressive strength of the cement paste samples with the addition of spent FCC catalysts has been strengthened by the number of works, such as [7] (pp. 103–108). This phenomenon might be attributed to the vital pozzolanic activity of spent catalysts, identified in [13]. Pozzolanic activity is the ability of a material to react with $Ca(OH)_2$ in the presence of moisture to form additional CSH gel in the system, thus contributing to compressive strength gain. Such behavior is promoted by the typical pozzolanic properties of spent FCC catalysts, i.e., aluminosilicate composition and high specific surface area.

The deterioration of the flexural strength of cement paste samples in relation to the increasing spent catalyst addition seems to be caused by the porous structure of the respective samples, as has been investigated through SEM analysis. Accordingly, the interphase transition zone (ITZ) reveals a lack of adhesion between the spent catalyst particles and CSH gel. This might be associated with the poor binding provided by the significant consumption of water by spent catalyst.

The results of water absorptivity of cement pastes indicated that spent FCC catalysts, while substituting 10% and more of cement, generally promote the water absorptivity of the respective paste samples. This finding is in accordance with [6] (pp. 111–118), and might be attributed to the fact that those samples tend to dry up, again as the catalyst provides high water absorption and thus also prompts water content reduction in the system. Moreover, such behavior seems to be strengthen by the low w/b ratio used to prepare the mixes.

Overall, based on the preliminary exploration of the possibility of using spent FCC catalysts as a pozzolanic additive to cementitious composites, this waste material was found to be a promising substitute for up to 20% of cement in primary cementitious composites, i.e., cement pastes, with the slight decrease in workability and increase in absorptivity acceptable from a construction materials quality viewpoint. It is vital that their addition results in higher compressive strength of hardened samples, whilst simultaneously decreasing the cost and carbon footprint arising from the cement industry. Therefore, the obtained results, combined with the conducted research into the applicability of spent FCC catalysts in cement mortars described in [14], allow us to conclude on the rightness of further research into using spent FCC catalysts from the Polish petrochemical industry in cementitious composites. The authors have to perform planned future studies in terms of investigating the impact of the addition of spent FCC catalysts on the properties of cement mortars. The research will include purification of spent catalysts from pollutants, and toxicity analyses of the resulting materials. The pozzolanic activity of spent catalysts and the setting time of related binders will be also measured. Moreover, other spent catalysts and petrochemical wastes, i.e., molecular sieves, will be investigated regarding such applicability.

5. Conclusions

On the basis of the conducted research, the following main conclusions may be drawn:

- Spent FCC catalysts derived from the Polish petrochemical industry reveal the potential to be recycled as a sustainable resource material with pozzolanic properties for cement substitution in cementitious composites. However, in terms of assessing their impact on the properties of cementitious composites more extensively, further research activity is planned, to be carried out on cement mortars by the authors.
- According to the research results, this material, while substituting 0–20% of cement, contributed to enhancement of the compressive strength of cement paste samples by up to 36% and 17%, respectively, on the 7th and 28th day of curing. Despite the fact that the workability, flexural strength and water absorptivity of the resulting composites are slightly deteriorated, they are still acceptable from a construction materials quality viewpoint. Moreover, these factors may potentially be minimized by using appropriate plasticizing admixtures.
- The recycling of ORW in the construction sector, if achieved, will contribute to numerous benefits such as decreased CO_2 emissions, natural resource protection and cost savings, whilst solving ORW utilization issues. Considering this, the correctness of further research regarding such an application of ORW is clearly underlined.

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