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# Sustainable utilization of cooper post-flotation waste in cement composites

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## Abstract

The current way of managing the copper ore flotation waste is by placing it in waste neutralization facilities. However, flotation waste has great potential in application in cement composites. The article presents the detailed characteristics of post-flotation waste (PFW) and three types of cements: CEM I, CEM II/B-V, and CEM III/A, 42.5 MPa class. The post-flotation waste added for 20% of the cement mass increase the water demand to obtain the standard consistency. The highest pozzolanic activity was noted for mortars made of Ordinary Portland Cement and cured at 20°C. The lower curing temperature, i.e. 10°C, delays the hydration reaction, extends setting time, and reduces compressive strength. The conducted tests showed that the specimens produced from CEM I and PFW have the highest compressive strength (after 28 and 90 days), which means that PFW does not react with silica fly ash (from CEM II/B-V) and granulated blast furnace slag (from CEM III/A). The reaction of the waste with the components of the Portland clinker is preferred. The performed studies proved that the utilization of copper post-flotation waste allows for the development of sustainable and durable composite made of CEM I and indicated the possibilities of further testing of waste, in the direction of its use as a mineral additive for concrete.

**Keywords:** cement composite; recycling; post-flotation waste (PFW); initial setting time; pozzolanic activity; compressive strength.

## 1. Introduction

Waste management of solid state becomes an area of interest for many scientists. The copper ore post-flotation tailings produced by froth flotation are a mixture of water, ground rocks, and chemical reagents and represent 95–99% of crushed ores; this means that for each ton of copper obtained through froth flotation, 151 tons of tailings are generated. Globally, mining tailings occur at a rate of five to fourteen billion tons per year. Although there are several tailings treatments to recover valuable elements, such as leaching, bioleaching, and froth flotation, these treatments only partially help the severe environmental impact of mining waste deposits [1]. Post-flotation waste (PFW) is produced from the extraction of metal ores subjected to the enrichment process. The mining industry's auxiliary products represent huge stocks of untapped resources that have consumed enormous amounts of energy to extract. New technological solutions, taking into account the chemical composition of industrial waste, create conditions for its disposal. The annual amount of waste generated in Poland by the mining industry is estimated at approx. 70 million tons.

The building materials industry is particularly interested in the management of solid waste with standardized properties. The most popular types of waste include silica or calcareous fly ash, granulated blast furnace slag, or silica fume [2,3]. With the progress of construction development and greater environmental awareness of the world, new types of mineral additives are sought [4–7]. Along with the progress in the development of construction and the growing environmental awareness of the world, new types of mineral additives are sought, such as oil refinery waste, waste foundry sand (WFS), coal bottom ash (CBA), cement kiln dust (CKD), wood ash (WA). The use of waste as a concrete additive has a double benefit. Firstly, it indicates a new type of waste management, and secondly, has a direct impact on environmental protection [8]. The partial substitution of clinker (the main component of the cement) reduces the amount of $CO_2$ produced by reducing the consumption of the calcined clinker [9]. Many scientists are trying to find new types of waste that could potentially contribute to reducing clinker consumption. An additional advantage of such research is the identification of new solutions in the field of waste management [10–12]. A lot of studies indicate that there is a need for a new type of additive for cement mortars. To ensure sustainable, cost-effective cement production in the 2020s, the industry needs to change. The most important challenges facing the industry are the urgent need to reduce $CO_2$ emissions and improve energy efficiency. The most effective methods of producing ecological, environmentally and economically sustainable cements of the highest quality are (a) the use of alternative, low-emission fuels and (b) the development of new recipes and methods of cement production - which boils down to the use of materials that do not need pre-treatment (thermal, chemical, mechanical) [13]. An example is the use of copper slag [14]. However to introduce the copper slag into cement mortars, it must be firstly activated by alkali [15] or mechanically [16]. The management of solid waste resulting from the extraction of valuable metallic and energy raw materials focuses mainly on waste management by placing it in treatment facilities [17]. However, further investigations are being carried out on the potential application of mining waste in the building materials industry, in particular cement composites [18]. As suggested by Rosado et al. [19] the application of copper waste as a construction material will reduce the consumption of natural raw materials for the production of building materials. The authors [19] concluded that according to European regulations, copper mining waste has the potential to replace part of the cement, or be a substitute for fine aggregate or constitute a mineral additive to mortar (composite). On the other hand, according to de Bastos et al. [20] the use of the copper waste as a filling aggregate (for the construction sector) is not frequently considered due to the need to stabilize the waste to reduce its danger.

The research conducted so far concerns the use of post flotation waste (PFW) in cement mortars [21–23], in the concrete [24–26], and in the ceramic products [27]. Based on the literature review, the Authors found that the use of waste in construction may have the following consequences: immobilization of heavy metals, energy-intensive pre-treatment, comparable or higher compressive strength, increase in composite density, increase in workability, reduction of surface water absorption [28,29]. As suggested by [30,31] the mortar or concrete containing tailings as fine aggregate is characterized by a higher percentage of water absorption due to the capillarity and higher specific surface area of the waste. Another option for the utilization of post-flotation waste is its use in geopolymer mixtures, after their activation with an alkaline solution [29,32,33]. As reported by Rajczyk [34] preliminary studies indicate that flotation waste can be used in some mining technologies, for example for grouting in caving area, filling post-exploitation, and as a component of backfill mixes, containing the binder.

The main aim of this study is to determine whether copper ore flotation waste could be a component of cement composites. There is no evidence in the literature for the use of flotation wastes for cements with varying clinker content. Although this type of material is well established, its effect on the chemical, physical and mechanical properties of cement composites using three different types of cement i.e. Portland cement, Portland-composite cement containing siliceous fly ash and blast furnace slag cement has not been extensively studied. It is interesting to find a resource consuming component of cement composite. This paper reports the results of chemical, mineralogical, and physical properties of three types of cements and post-floatation waste. The experimental program also includes tests of the initial setting time of cement pastes and calculations of the pozzolanic activity of cement mortars curing under two different temperature conditions (10 and 20$^{o}$C). The results focus on the selection of the appropriate type of cement as the basic mineral binder to which the post-flotation waste can be added. The effectiveness and limitations of the considered waste are discussed in detail. The presented research is of a pilot nature as an indication of a potential new way of managing copper ore flotation waste.

## 2. Materials and methods

In these studies, the copper ore flotation waste from the "Żelazny Most Waste Treatment Facility", owned by KGHM Polska Miedź, was used. The samples came from the Lubin Enrichment Plant and were classified as code 01 03 81 - wastes from flotation enrichment of non-ferrous metal ores other than those mentioned in 01 03 80 (wastes from flotation enrichment of non-ferrous metal ores containing dangerous substances). This means that considered waste has not been classified as hazardous [35,36]. The research included the preparation of cement pastes and cement composite by using three types of cements from the company 'Lafarge", Poland: CEM I 42.5R (Ordinary Portland cement), CEM II/B-V 42.5R (Portland-composite cement containing siliceous fly ash) and CEM III/A 42.5R (blast furnace slag cement) by the standard [37]. The tests concerned the preparation of samples, with and without post-flotation waste in the amount from 5% to 40% of the cement mass.

The first stage of studies concerned the determination of the characteristics of used materials. Chemical composition analysis was performed using X-ray fluorescence (XRF WDXRF Axios mAX Spectrometer with a 4kW Rh tube by PANalytical). X-ray diffraction analysis has been performed, which allows for the recognition of the phases occurring in the waste. It used a Philipps X'Pert Pro diffractometer. A copper tube (CuKα = 1.54178 Å) was used as a source of the X-ray emission. X'Pert Highscore software was used to process the diffraction data. Identification of mineral phases was based on the PDF-2 database formalized by JCPDS-ICDD. The particle size distribution of the microspheres was analyzed by a laser particle analyzer (Helios/R, Sympatec GmbH Germany). Laser diffraction is a standardized method according to the International Standard ISO 13320 [38] and it is used for the determination of particle size distribution. The analyzer applies to rapid and automatic particle size analysis of solids by dry method. The range of operation of the analyzer varies from 0.1 to 3500 μm. A computer connected to the laser grain size measurement gives characteristic diameters: $D_{10}$, $D_{50}$, $D_{90,}$ and $D_{mean.}$ The loss on ignition (LOI) was identified by EN 196–2 [39].

In the second stage of research, the identification of the initial setting time of cement pastes, by EN 197-1: 2012 [37], was performed. The investigation was carried out for three types of cements cured at two temperatures (10 and 20 ˚C) with the addition of PFW in the following amounts: 0%, 5%, 10%, 20%, and 40% of the cement mass. The total number of considered pastes was equal to 30. To determine the initial setting time of cement pastes, the standard consistency was tested each time.

The pozzolanic activity was defined as the percentage ratio of the compressive strength of the standard cement mortar, made with 75% (337.5g) by weight of the reference cement and 25% (112.5g) by weight of the PFW wastes potential additive, and tap water (225 g), (the water-binder (w/b) ratio was 0.50) to compressive strength containing 100% reference of the cement samples used in these studies. The degree of pozzolanic activity was determined by EN 450-1: 2009 [40]. The compressive strength of samples with dimensions of 40 x 40 x 160 mm was analyzed after 28 and 90 curing days. The mortar specimens were stored in a water bath at two constant temperatures: 10 and 20°C. The compressive strength was determined in according to EN 197-1 [37]. The composition of cement pastes and cement mortar is shown in Table 1.

***Table 1.*** *Composites of pastes and mortars prepared for testing*

| Types of samples | Cement[1] [g] | PFW [g] | PFW [%] | Sand [g] | Water [g] |
|---|---|---|---|---|---|
| PASTES | 450.0 | - | 0 | - | Determined experimentally. The results are presented in table 5. |
| | 427.5 | 22.5 | 5 | - | |
| | 405.0 | 45.0 | 10 | - | |
| | 360.0 | 90.0 | 20 | - | |
| | 270.0 | 180.0 | 40 | - | |
| MORTARS | 450.0 | - | 0 | 1350 | 225 |
| | 337.5 | 112.5 | 25 | 1350 | 225 |

[1)] cement CEM I or CEM II/B-V or CEM III/A was used

## 3. Results and discussion

### *3.1. Chemical composition of materials*

The analysis of the chemical composition allows determining the main components of copper flotation waste and used cements. Table 2 shows the results of the XRF analysis.

***Table 2.*** *Chemical composition of materials (by % weight) determined via XRF*

| Components | PFW | CEM I 42.5R | CEM II/B-V 42.5R | CEM III/A 42.5R |
|---|---|---|---|---|
| **$SiO_2$** | 61.58 | 15.74 | 22.97 | 26.9 |
| **CaO** | 18.93 | 67.86 | 52.77 | 54.29 |
| **$Al_2O_3$** | 5.57 | 4.58 | 10.69 | 6.85 |
| **$SO_3$** | 3.12 | 3.96 | 3.12 | 3.65 |
| **MgO** | 2.82 | 1.49 | 1.64 | 4.00 |
| **$K_2O$** | 2.28 | 0.77 | 1.28 | 0.45 |
| **$Fe_2O_3$** | 2.01 | 4.20 | 5.19 | 2.29 |
| **CuO** | 0.88 | 0.03 | 0.02 | 0.02 |
| **$Cl^-$** | 0.54 | 0.10 | 0.15 | 0.05 |
| **$TiO_2$** | 0.52 | 0.47 | 0.83 | 0.42 |
| **$Na_2O$** | 0.40 | 0.17 | 0.73 | 0.43 |
| **MnO** | 0.28 | 0.16 | 0.09 | 0.34 |
| **BaO** | 0.26 | 0.04 | 0.06 | 0.05 |
| **PbO** | 0.22 | - | - | - |
| **$Cr_2O_3$** | 0.13 | 0.05 | 0.02 | 0.02 |
| **$P_2O_5$** | 0.10 | 0.17 | 0.17 | 0.08 |
| **SrO** | 0.10 | 0.14 | 0.06 | 0.07 |
| **$ZrO_2$** | 0.07 | 0.02 | 0.03 | 0.01 |
| **ZnO** | 0.04 | 0.05 | 0.14 | 0.02 |
| **$Co_3O_4$** | 0.02 | - | - | - |
| **Total mass** | 100.00 | 100.00 | 100.00 | 100.00 |

Copper ore flotation waste is characterized by a high content of silicon oxide (61.6%) compared to the total weight of the tested material, Table 2. The silica behavior is more complex and it is related to pozzolanic activity. Reactive silica plays an important role in the cement hydration process, creating one of the reaction products - hydrated calcium silicates. The formation of a new chemical compound (CSH phase) in a longer maturation period increases mechanical strength. Test results [41] show that waste with high silica content (> 75%) and low calcium content (<10%) when mixed with clinker in small proportions (<5%) allows obtaining compressive strength corresponding to the cement class, 42.5N.

The presence of this oxide in flotation waste equals only 18.9%. An important component of cements is aluminum oxide, which is involved in the formation of calcium aluminosilicates. A potential problem with application of copper ore flotation waste in cement composites may be the proportion of copper oxide, which according to Lin et al. [42], visibly lowers the hydration process. The PFW also contains small amounts of $Na_2O$ (0.4%) and $P_2O_5$ (0.1%).

Taking into account the results presented in Table 2, it can be concluded that the content of copper oxide (CuO) and lead oxide (PbO) are 0.88% and 0.22%, respectively. The content of these elements is related to their dominance in post flotation waste, to compare, to other heavy metals in form of oxides. According to the regulations [43], the use of post-flotation tailings depends on the limit values depends for leaching of the heavy metals, which may pose a potential threat to the natural environment. The limits contained in the soil for Cu and Pb is 100 mg/kg. Limits of heavy metal content for soil according to the regulation [44] are presented in Table 3.

***Table 3.*** *Limits of heavy metal content for soil* [44]

| Component: | [mg/kg] |
|---|---|
| **Zinc (Zn)** | 300 |
| **Cadmium (Cd)** | 2 |
| **Cobalt (Co)** | 20 |
| **Copper (Cu)** | 100 |
| **Molybdenum (Mo)** | 10 |
| **Nickel (Ni)** | 100 |
| **Lead (Pb)** | 100 |

As suggested by Rosado et al. [19], copper mining waste has the potential to replace part of the cement and act as a hydraulic binder, either as fine aggregate or as an additional mineral. In mortars, there is the freedom to add copper residues in any aspect, but in concrete, certain limits in terms of particle size distribution must be respected. In both cases, its application will depend on the leaching values of the heavy metals of post flotation waste. Based on EN 206:2014 [45], the chloride content in concrete without steel reinforcement should be max. 1.0%, for concrete with reinforcement – max. 0.40%; with prestressing steel reinforcement – max.0.2% of the cement mass.

### *3.2. X-ray diffraction of materials*

The XRD method was applied for the identification of the phase composition of the three types of cement and post-flotation waste. The results of the mineralogical composition (in the form of a diffraction pattern) of cement samples and post flotation waste are presented in Figure 1 and Figure 2, respectively.

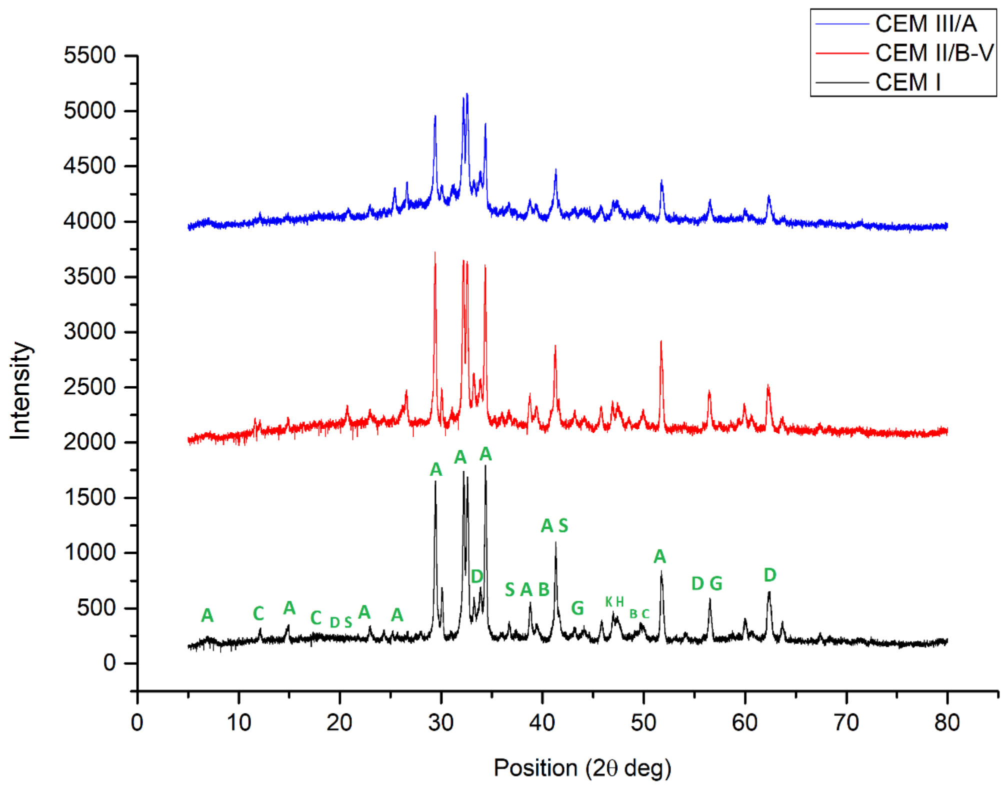



***Figure 1.*** *XRD pattern of tested cements.*

As demonstrated in Figure 1, XRD are the presence of the following phases: Alite (A), Belite (B), Brownmillerite (C), Tricalcium aluminate (D), Calcite (K), Gypsum (G), Calcium sulfate hemihydrate (S) and Anhydrite (H). The percentage content of mentioned phase is presented in Table 4. Calcite ($CaCO_3$) is the basic material for the production of cements. Additionally, calcite is used as a flux in the production of blast furnace slag, a component of blast-furnace cement. Taking into account the phase composition of cements, gypsum plays the role of a setting time regulator. The high content of this phase is in ash Portland cement. It delays the initial setting time compared to other cements [46].

***Table 4****. The phase composition of cements made based on X-Ray Diffraction (Rietveld Refinement)*

| **Phase** | **Chemical formula** | **Percentage of phases** | | |
|---|---|---|---|---|
| | | **CEM I** | **CEM II/B-V** | **CEM III/A** |
| Alite | $C_3S$ ($3CaO \cdot SiO_2$) | 67.4 | 58.9 | 35.8 |
| β-Belite | $C_2S$ ($2CaO \cdot SiO_2$) | 3.2 | 6.9 | 18.4 |
| Brownmillerite | $C_4AF$ ($4CaO \cdot Al_2O_3 \cdot Fe_2O_3$) | 11.7 | 7.3 | 7.5 |
| Tricalcium aluminate | $C_3A$ ($3CaO \cdot Al_2O_3$) | 5.5 | 8.9 | 6.4 |
| Periclase | $MgO$ | 0.6 | 0.2 | 0.1 |
| Calcite | $CaCO_3$ | 7.8 | 9.0 | 11.0 |
| Gypsum | $CaSO_4 \cdot 2H_2O$ | 0.6 | 7.1 | 4.6 |
| Calcium sulfate hemihydrate | $CaSO_4 \cdot 0.5(H_2O)$ | 2.9 | 0.6 | 10.7 |
| Anhydrite | $CaSO_4$ | 0.2 | 1.3 | 5.6 |

Table 4 shows the phase composition of cements obtained with XRD (Rietveld Refinement) tests [47]. For every considered cement, the main clinker phases are alite, belite, brownmillerite, and tricalcium aluminate.

The total content of these phases in Portland cement equals 87.8%, in ash Portland cement is 82%, and in blast furnace cement equals 68.1%. The high content of alite ensures high early compressive strength (up to 28 days). On the other hand, in the case of CEM III/A, the highest content of belite contributes to the increase of long-term strength (after 90 days).

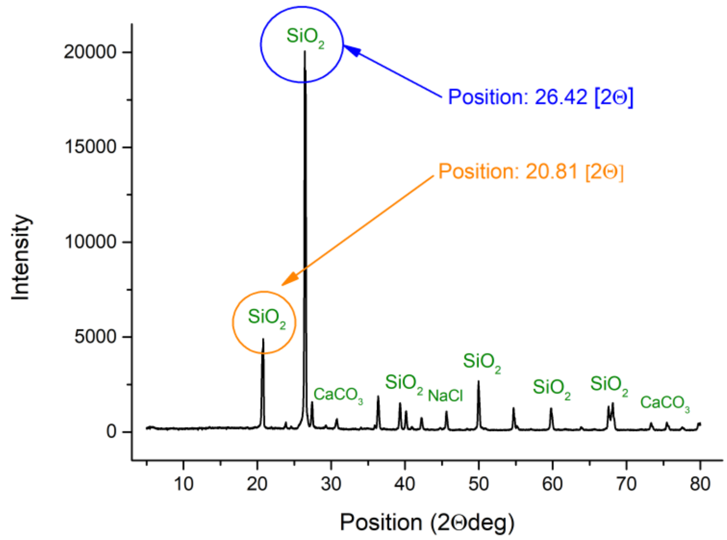



***Figure 2.*** *XRD pattern of the post-flotation waste.*

As shown in Figure 2, the phase composition of the PFW indicates the highest crystalline $SiO_2$ presence. The wide range of reflections in the pozzolana diffraction pattern, in the range of 22-35 °2Θ, indicates the presence of active silica, which corresponds to dehydrated silica gel. This may have a positive effect on the reactivity of the tested material in the cement composite. On the other hand, the band in the range of 20-22 °2Θ indicates the presence of crystalline silica (crystalline quartz), which hurts the pozzolanic reactivity of the material [48]. Another detected ingredient is calcium carbonate. It is a component of the clay rock left over from the copper ore flotation process. Calcium has a beneficial effect on the hydration process of cement mortars. The above conclusion was formulated based on the research results of Ma et al. [49]. The scientists proved that the $CaCO_3$ can promote the early hydration of cement and can react with $C_4A_3\acute{S}$ to form hemicarbonate ($4CaO{\cdot}Al_2O_3{\cdot}0.5CO_2{\cdot}12H_2O$, Mc) and monocarbonate ($4CaO{\cdot}Al_2O_3{\cdot}CO_2{\cdot}11H_2O$, Mc), which can stabilize ettringite and change the pore structure of cement. Additionally, XRD analysis showed the presence of halite (NaCl). The minerals occurring in Lower Silesia (the place of taking the tested waste) may be rich in halite, which is not recovered in the flotation process. Chloride ions initially seal the structure of the cement composite, increasing the compressive strength.

However, over time, the hydration products can expand in volume by being incorporated into the structure of the cement matrix. The effect of this phenomenon will be the formation of microcracks in the structure of the material, which will lead to a rapid reduction in compressive strength. Moreover, the high content of chloride ions may harm the durability of the reinforcement in cement composites.

### *3.3. Physical parameters of materials*

The following chapter includes tests of the physical parameters of cements and copper ore flotation waste. The basic parameters are summarized in Table 5. Copper ore flotation waste contains the smallest amount of burnt organic substances, and thus is characterized by the lowest value of a loss on ignition (1.1%). The ash Portland cement has the highest value of a loss on ignition (4.2%) due to the participation of the silica fly ash in the composition of cement. Fly ash is obtained by mechanical or electrostatic precipitation of ashes from flue gases from coal dust combustion in power boilers. European standard EN 196-2:2013 [39] reports the maximum loss on ignition for fly ash equal to 5%. As shown in Table 5, the mentioned value did not exceed for any of the tested materials. For example, according to NRMCA [50], corrosion initiates when the concentration of chlorides exceeds a threshold concentration at the reinforcing steel. Although these chloride concentration values can vary, they are typically in the range of 0.05 to 0.1% of the weight of the concrete—about (1.2 to 2.4 kg/m$^3$), or ~0.4 to 0.8% of the weight of cement (based on the assumption of ~500 lb/yd$^3$ [297 kg/m$^3$] of cement). In turn in Europe, the maximum permissible total chloride ion levels in fresh concrete are 0.4% (by % weight of cement) for reinforced concrete and 0.1% for prestressed concrete. These limits apply irrespective of whether or not the concrete is exposed to external chlorides [51].

***Table 5.*** *Physical parameters of PFW and the three types of cements*

| Parameters | LOI [%] | BET [m$^2$/g] | Pore volume [cm$^3$/g] | VDM$^{*1}$ [µm] | $D_{50}$ [µm] | Span$^{*2}$ [-] |
|---|---|---|---|---|---|---|
| PFW | 1.1 | 2.970 | 0.0015 | 149.16 | 149.13 | 1.37 |
| CEM I | 3.1 | 1.712 | 0.0008 | 21.59 | 20.74 | 2.74 |
| CEM II/ B-V | 4.2 | 2.246 | 0.0011 | 14.73 | 14.88 | 3.00 |
| CEM III/A | 1.4 | 1.594 | 0.0008 | 21.72 | 12.79 | 2.15 |

$^{*1}$VDM - Volume Mean Diameter

$^{*2}$Span - Volume-based size distribution (($D_{90}$-$D_{10}$)/$D_{50}$)

The BET (Brunauer, Emmett, and Teller) theory was used to evaluate the specific surface area results expressed in units of area per mass of sample (m$^2$/g). The technique is widely used for most materials and referenced by several standard organizations such as ISO, USP, and ASTM. The copper ore flotation waste has the largest specific surface area equal to 2.970 m$^2$/g. The smallest values were obtained for CEM III/A (1.594 m$^2$/g) and CEM I (1.712 m$^2$/g). A large specific surface area may accelerate physicochemical reactions in materials. Furthermore, the total pore volume of the samples was determined by the BET analysis. According to data presented in Table 5, all cements and waste have a small pore volume. The similar pore volume values eliminate the influence of the void size on the design of mortar mixes and do not change the water demand. The volume means diameter for cements used in this study ranges from 14.88 to 21.72 µm, and for PFW is 149.16 µm.

The comparison of copper ore flotation waste and cements was conducted by using laser analysis. Figure 3 shows the particle size distribution curves of cements and flotation waste. The first parameter determined in the laser analysis was the $D_{50}$, Table 5. It is defined as the median size i.e. the size that splits the size distribution with half above and half below the specified diameter [38]. The $D_{50}$ parameter of the PFW was equal to 149.13 µg and was 10 times larger than the tested cement samples. When discussing the median results, the spread of the results (Span) is an important parameter [52]. Span parameter shows the width of the size distribution. If the span is closer to zero, it means the graininess is uniform. The span of a volume-based size distribution gives an indication of how far the 10 percent and 90 percent points are apart, normalized with the midpoint. Based on the calculated span, it can be stated that the waste is more homogenous than considered cements.

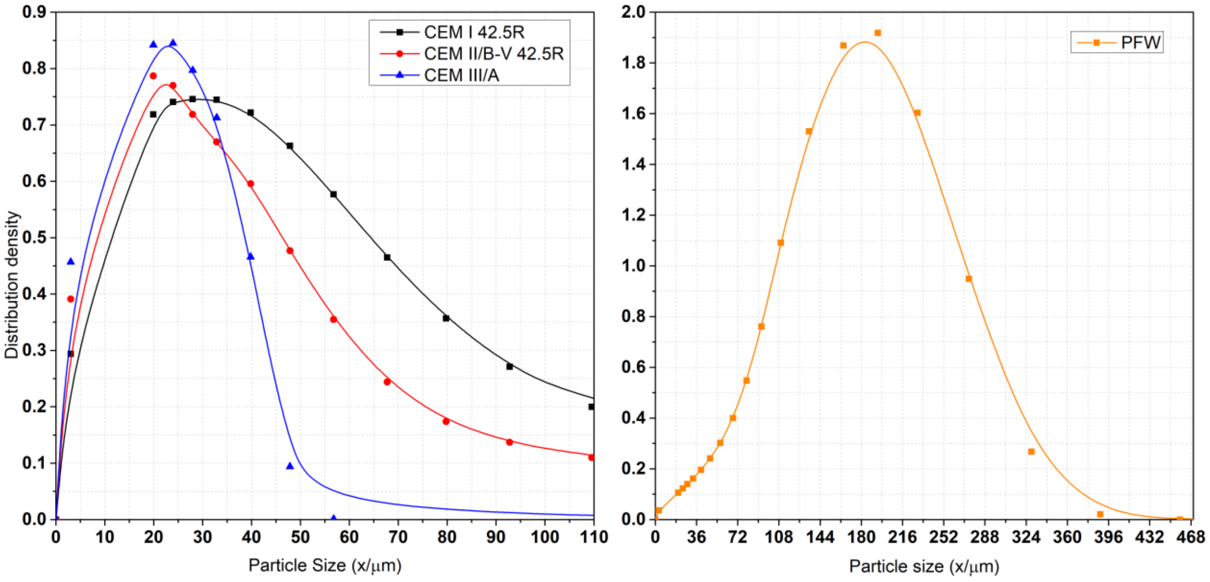



***Figure 3.*** *Particle size distribution of PFW and the three types of cement*

The particle size distribution curves presented in Figure 3, indicate that three types of cement have a particle size in the range are respectively: to 120 μm (CEM I 42.5R), 180 μm (CEM II/B-V 42.5R), and 62 μm (CEM III/A 42.5R). While the PFW particle size is up to 420 μm and can be described as strictly homogenous. The conducted tests of post-flotation waste concerned material taken from the landfill without prior mechanical treatment. Taking into account the cumulative distribution, a relatively large fraction of the cement particles (up to 56.1% for CEM I 42.5R; 60.84% for CEM II/B-V 42.5R and 71.19% for CEM III/A 42.5R) is less than 18 μm. For PFW particles, about 5.58% have a smaller diameter than 18 μm. The percentage of grains of PFW in the range from 18 μm to 100 μm and 100 to 500 μm are respectively: 21.28% and 73.04% of the total mass.

As reported [25] that the mineral phases in the waste have different densities and water absorption, which is also significantly influenced by the size of their particles. In general, concrete includes coarse aggregate and fine aggregate, but tailings are merely used as partial or full replacements of fine aggregate since their particles are fine with a diameter of less than 1 mm. The physical properties of tailings have a significant impact on the workability, density, dimensional stability, strength, and durability of concrete [31,53]. The studies [54,55] suggest that the use of waste as a substitute for fine aggregate increases the density of fresh mixes because waste has a higher specific gravity compared to the specific gravity of natural sand.

### *3.4. Standard consistency*

The standard consistency was determined by using the Vicat apparatus by EN 196-3 [56]. The amount of water needed to obtain the standard consistency was determined based on multiple penetration tests of the needle in cement pastes for different water content. The results for the three types of cements with 5%, 10%, 20%, and 40% of PFW replacement for cement mass are summarized in Table 6.

***Table 6.*** *Water demand for cement pastes with copper ore flotation waste*

| Amount of waste [% mas. cem.] | Water needed to obtain standard consistency [g] (Percentage of water in the mineral binder) |
| --- | --- |

| | CEM I 42.5R | CEM II/B-V 42.5R | CEM III/A 42.5R |
|---|---|---|---|
| 0 | 146.2<br>(32.5%) | 159.5<br>(35.4%) | 152.1<br>(33.8%) |
| 5 | 148.7<br>(33.0%) | 157.6<br>(35.0%) | 155.4<br>(34.5%) |
| 10 | 157.4<br>(35.0%) | 158.3<br>(35.3%) | 157.9<br>(35.1%) |
| 20 | 155.1<br>(34.5%) | 157.3<br>(35.0%) | 156.8<br>(34.8%) |
| 40 | 127.3<br>(28.3%) | 128.6<br>(28.6%) | 129.3<br>(28.7%) |

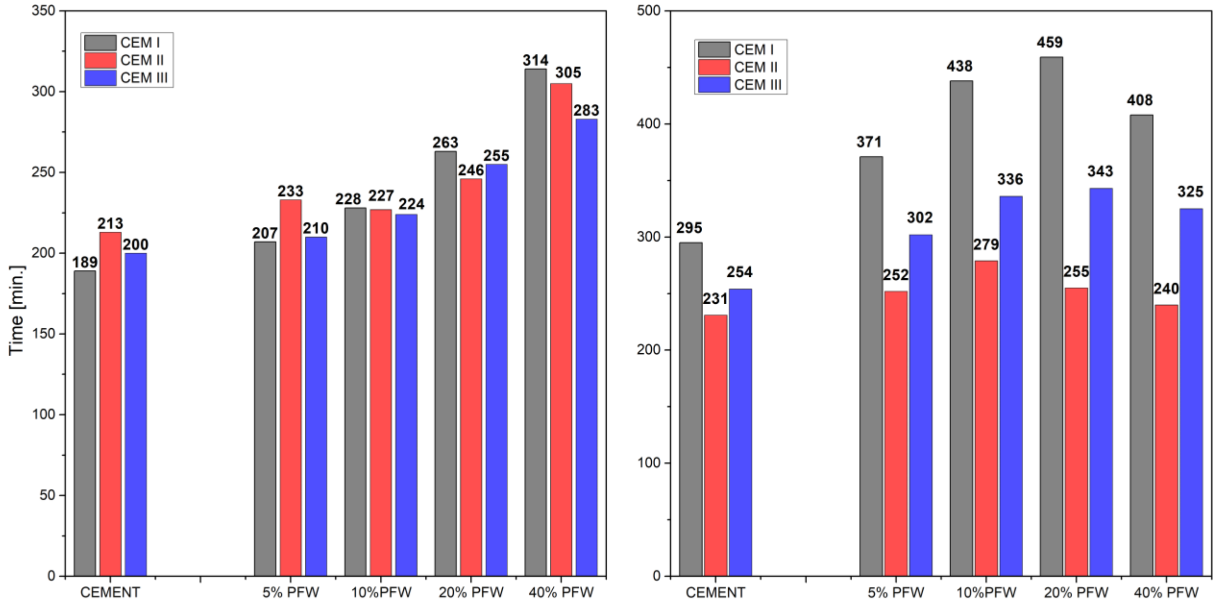
In the case of Portland cement, the amount of water needed to obtain the standard consistency increases until 20% of cement replacement by post-floatation waste. The water demand is higher, up to 20% of the waste, in the case of pastes made of CEM I and CEM III compared to the reference sample (without PFW). Cement with the addition of silica fly ash is characterized by the largest specific surface area (BET) and LOI of the tested cements, which results in the highest water demand (water demand is much higher for fly ash than for PFW). Only for 40% of PFW, a slight increase in the water demand is visible in the case of CEM II/B-V cement compared to pastes made with other cements. The increase in the amount of water demand ranges from 1.7% to 7.7% compared to the reference sample. If 40% of the cement is replaced, the amount of water needed to achieve standard consistency is reduced. The observed relationship is due to the lower waste water demand compared to Portland cement. As demonstrated in Table 6, the two types of cement: CEM II/B-V 42.4R and CEM III/A 42.5R needs more water to reach the standard consistency compared to CEM I 42.5R. The increase is respectively: 9.1% (for CEM II/B-V 42.5R) and 4.0% (for CEM III/A 42.5 R). The reason for the increased demand for water is the presence of silica fly ash in the cement composition. CEM II/B-V is characterized by the high value of a loss on ignition (Table 5), which means that it absorbs more water than cement without additives.

The addition of copper ore flotation waste (PFW) to the cement pastes in the amount of 5% to 40% decreased the amount of water, respectively: by 12.99% (for CEM I 42.5R), by 19.37% (for CEM II/B-V 42.5R) and by 14.99% for CEM III/A 42.5R compared to the amount of water and water introduced into the cement pastes without the use of the test material.

After mixing the cement with water, the absorption of polar water molecules on the surface of the binder grains (cement and waste) takes place, which through dissolution - hydrolysis (decomposition) of active particles of gypsum, calcium aluminate, and alite, and after exceeding the PFW in the amount of 10% of the cement mass, affects the water absorption as a result of an increase in the degree of fragmentation of the tested material. At the beginning of the process, an almost entirely amorphous layer is formed composed mainly of calcium sulphate, calcium aluminate and a hydrated C-S-H phase. The products cause the consolidation of a more or less liquid grout. Therefore, an increase in the PFW content above 10% of the mass of cement probably causes an increase in water demand.

### *3.5. Initial setting time*

The initial setting time was determined by EN 196-3 standard [56] at two temperatures: 10 and 20°C. Pastes mixtures with three types of cement and four rates of cement substitution with copper ore floatation waste (5%, 10%, 20%, and 40%) were investigated. For every test, the time of initial water contact with cement was recorded. The results of the initial setting time are shown in Figure 4. The black columns refer to CEM I 42.5R, the red columns are related to CEM II/ B-V 42.5R, and the blue ones to CEM III/A 42.5R.




**A. Temperature: 20°C** **B. Temperature: 10°C**

***Figure 4.*** *The setting time of pastes at two temperatures: A) at 20°C, B) at 10°C*

For ordinary Portland samples (CEM I 42.5R), cured at 20˚C, the initial setting time extended from 189 to 314 minutes with the increasing amount of added waste (Fig. 4a). The addition of even a small amount of waste (5%) increased the time needed for setting by 10%. Additionally, with the replacing 40% mass of ordinary Portland cement with PFW, the initial setting time was prolonged i.e., increased by 66%. Ash Portland cement takes longer to begin the setting compared to Ordinary Portland Cement (Fig. 4a). However, the maximum replacement of CEM II/B-V 42.5R by flotation waste delayed the initial setting time by 43%, which is a lower value compared to CEM I 42.5R. The replacement of part of the blast-furnace cement with flotation waste also caused a delay in setting time, in a similar way to the Portland cement (Fig.4a). However, the delay is not as high as for CEM I 42.5R (with 40% PFW the delay equals 42%). In percentage terms, PFW has the least impact on CEM III/A 42.5R, at 20°C.

By summarizing, at a temperature of 20°C copper ore flotation waste delays the initial setting time. This is due to the solubility of the components in the cement composite. The second reason for delaying the setting time is the fragmentation of the material. The grains of waste are larger, so they have a smaller contact surface with the cement pastes. The larger size of waste grains, compared to cements, hinders physicochemical processes and slows down the chemical reactions that occur during the setting of cement composites.

The application of a low temperature (equal to 10°C) of hydration of cement pastes delays the initial setting time (Fig. 4b). It is related to the rate of chemical reactions. According to the Arrhenius formula [57], the temperature of the occurrence of chemical reactions has a direct, exponential effect on the cement hydration rate. The temperature factor greatly affects the setting time of considered samples. The results of the effect of temperature on the onset of setting time are summarized in Table 7. This table shows the percentage effect of the reduced temperature on the delay in the onset of setting time. A negative value indicates an acceleration of the onset of the setting time.

***Table 7.*** *Influence of curing temperature on the setting time of cement pastes*

| Type of the cement | 0% PFW | 5% PFW | 10% PFW | 20% PFW | 40% PFW |
|---|---|---|---|---|---|
| CEM I 42.5R | 56.08% | 79.23% | 92.11% | 74.52% | 29.94% |
| CEM II/B-V 42.5R | 8.45% | 8.15% | 22.91% | 3.66% | -21.31% |
| CEM III/A 42.5R | 27.00% | 43.81% | 50.00% | 34.51% | 14.84% |

The 40% share of copper ore post-flotation waste had the least influence on the beginning of setting time. Thus, it can be concluded that the addition of copper post-flotation wastes at a reduced temperature accelerates the initial setting time. The greatest impact of the lowered temperature is visible for Portland cement (Fig. 4b) because it is most sensitive to low temperatures. At 10°C, the components of cements have a difficult diffusing into the solution; therefore, the hydration reaction of cement pastes develops slower. For all cements, the greatest delay in the initial setting time occurred when 10% of the cement mass was replaced with copper flotation waste (Fig. 4b). The post-flotation waste may contain setting time initiation accelerators such as chloride or sodium ions and retarders such as copper or zinc ions. At 10% of post-flotation waste, setting time retarders have a greater effect than accelerators. Subsequent dosing of waste results in a greater effect of substances accelerating the initial setting time, which masks the negative effect of the ions delaying the onset of the setting time.

As suggested [58] the setting time of mortar extended when the tailings were incorporated as a replacement of fine aggregate, for the heavy metals in waste retarded the hydration of cement by forming a low permeability layer around cement clinker un-hydrated grains.

### *3.6. Pozzolanic activity – compressive strength*

The pozzolanic activity of the three types of cement mortars doped with PFW was determined according to European Standard 450-1 [40]. The mortar specimens were stored in water bath at two constant temperatures: 10 and 20°C. The compression tests of 50-mm mortar cubes were performed after 28 and 90 days of hardening. The total number of prepared samples was 72 (six mixtures × two temperatures × 2 times x three cubes per mixture). The results of average compressive strength (six samples) with an indication of the standard deviation (SD) are presented in Figure 5 and Figure 6. The SD of strength varies from 1.08 to 3.74. The strength activity index (expressed in %) was calculated as the ratio between the average compressive strength of the samples doped with PFW) to the average compressive strength of the control mortar beams. The values of computed indexes, for specimens cured at 20 and 10°C, are shown in Table 8 and Table 9, respectively

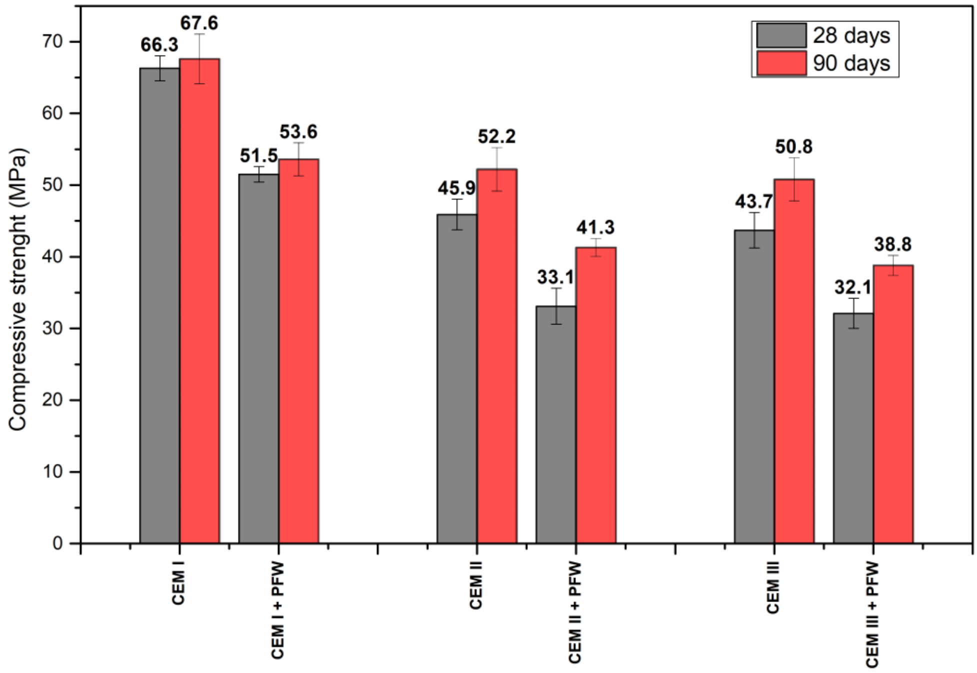



***Figure 5.*** *The average compressive strength of mortars cured at 20°C*

In the case of all cements, replacing 25% of the cement mass with copper ore flotation waste resulted in a decrease of the mortars strength, both after 28 and 90 days (Figure 5). All considered cements with the strength class 42.5 (minimum mortar strength after 28 days of hydration should be 42.5 MPa) were investigated. Portland cement is characterized by high early strength; therefore, after 28 and 90 days of hardening, the values of compressive strength were similar (increase by 2% in the control mortar and 4% in the PFW mortar). As shown in Figure 5, the addition of post-flotation waste decreased the strength of the mortars, but it did not reduce the class of Portland cement. The strengths of the mortars with PFW reached the value of 77.7% after 28 days and 79.3% after 90 days as compared to the control mortar (Table 8).

***Table 8.*** *The strength activity index for cubes cured at 20°C*

| Temperature | Curing age | CEM I 42.5R | CEM II/B-V 42.5R | CEM III/A 42.5R |
|---|---|---|---|---|
| 20°C | 28 days | 77.7% | 72.1% | 73.5% |
| | 90 days | 79.3% | 79.1% | 76.4% |

The composition of ash Portland cement mortars includes two mineral additives: silica fly ash and copper flotation waste. Silica fly ash retards strength gain over time. Initially, the ash is not reactive in the cement paste, thus a significant increase of compressive strength between 28 and 90 days was observed (Figure 5). The strength increase in the control mortar was 14% and in the PFW mortar 25%. However, copper ore flotation reduced compressive strength by 28% after 28 days and by 21% after 90 days of hardening. Finally, the mortars containing CEM II/B-V 42.5R and PFW did not reach the minimum cement class (Figure 5). The EN 450-1 standard [40] reports that at 28 days the mortar doped with additive should achieve a minimum of 75% of the strength of the control mortar, and after 90 days, 85% of the strength. In this study, the mentioned conditions are not met. However, the percentage strength differences are slightly lower than specified in the standard. The differences are

2.9% (at 28 days) and 5.9% (at 90 days). The strength reduction may be caused by poor compaction of the mortar mixture and the potential moisture of the sand or additional, undesirable components in the sand composition. The mortars made of CEM III/A 42.5R achieved the lowest values of compressive strength (Figure 5). The blast-furnace slag cement has the lowest summarizing amounts of alite and belite (Table 2), which are directly responsible for the early-age and later-age compressive strength gain (Figure 5). Moreover, according to the results of Rietveld Refinement [59], the slag cement has as much as 20.9% calcium sulphate in its phase composition (total amount of gypsum, anhydrite, and calcium sulfate hemihydrate). Sulphates delay the initial setting time and affect the strength increase.

Figure 6 shows the results of compression tests performed on samples stored at reduced temperature i.e., at 10°C. As in the case of the temperature of 20°C, the mortars with the addition of PFW obtained lower compressive strengths compared to the control mortars. The strength of mortars increased after 90 days by 11% and 18 %, respectively for CEM I and CEM I+PFW. The reduced temperature dropped the hydration reaction of the clinker phases.

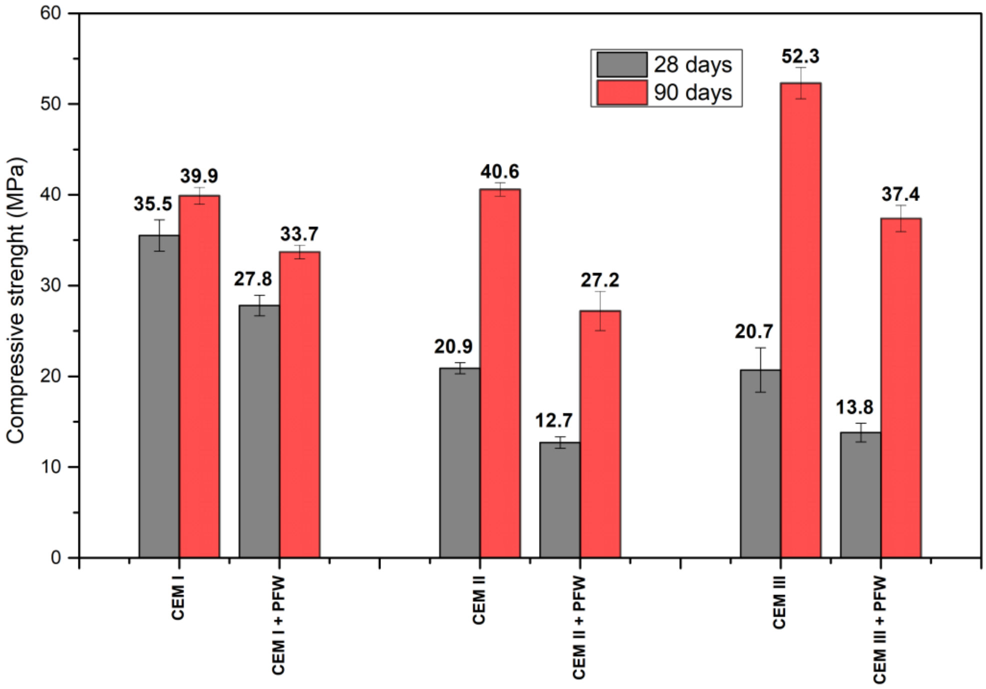



***Figure 6.*** *The average compressive strength of mortars cured at 10°C*

The copper ore flotation waste significantly influenced the compressive strength of the samples made with silica fly ash. Ash Portland cement contains the smallest amount of calcium oxide (Table 2), which inhibits the hydration reaction. Additionally, this cement has the highest amount of organic carbon, which also leads to a reduction of compressive strength (Figure 6). Unfortunately, the mortars molded using CEM II/B-V 42.5R did not reach the minimum compressive strength i.e., 42.5 MPa. Unfortunately, all samples cured at 10ºC did not reach the minimum compressive strength after 28 days i.e., 42.5 MPa. This is due to slower bonding and hydration reactions at reduced temperature. Low temperature reduces the rate of reaction, which directly translates into the strength of mortars.

*Table 9.* *The strength activity index for cubes cured at 10°C*

| Temperature | Curing age | CEM I 42.5R | CEM II/B-V 42.5R | CEM III/A 42.5R |
|---|---|---|---|---|
| 10°C | 28 days | 78.3% | 60.8% | 66.7% |
| | 90 days | 84.5% | 67.0% | 71.5% |

The highest increase of compressive strength between 28 and 90 days of hardening is visible for slag cement. The compressive strength of the control mortar after 90 days of hydration increased by as much as 153%, and with the addition of PFW, the strength increased by 171%. This means that a curing temperature equal to 10°C has a favorable effect on mortars made with CEM III/A 42.5R Nevertheless; these mortars did not reach the minimum compressive strength (42.5 MPa) at 28 days.

It is worth noting that ash Portland cement and blast-furnace slag cement have a much lower content of calcium oxide in their chemical composition. This is the reason for the inhibition of the reaction of the clinker phases, which are directly responsible for the gain of compressive strength. Copper ore flotation waste lowered the compressive strength, but in the case of pure Portland cement, it is possible to achieve values that meet the criteria of cement standards -it does not lower the cement strength class and achieves very similar pozzolanic activity values. The reduced temperature delays the initial setting time drops the hydration reaction and decreases the compressive strength.

*3.7. X-ray diffraction of pozzolanic mortars*

Pozzolanic mortars (with PFW) were subjected to the XRD test to identify the composite phase composition and to calculate the number of individual phases after 90 days of hydration at 20°C. The results of the X-ray analysis are shown in Figure 7. To determine the number of individual phases in cement composites, the Rietveld Refinement method was used and the results are presented in Table 10 for reference mortars and pozzolanic mortars.

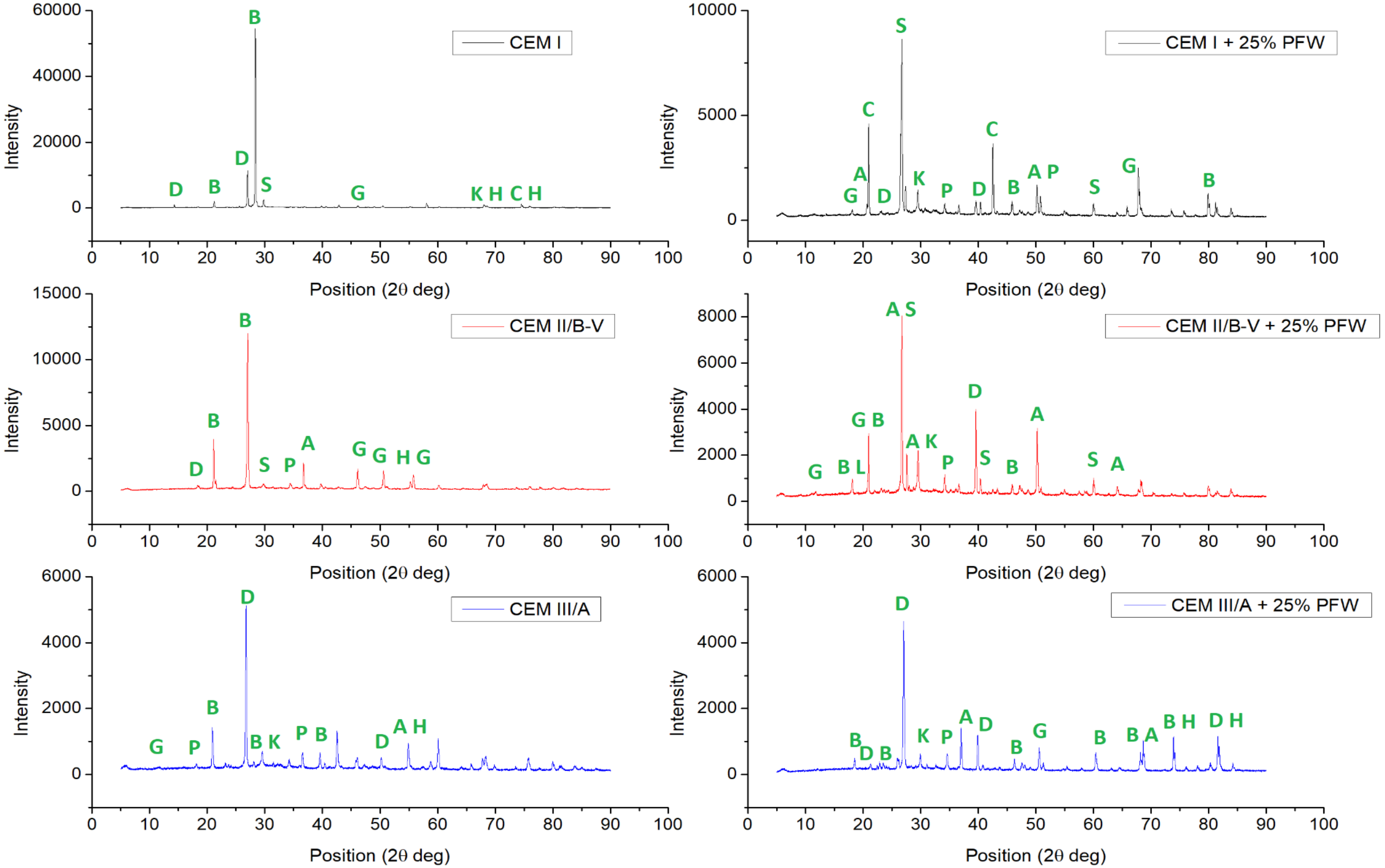



***Figure 7.*** *XRD pattern of the cement mortars with PFW after 90 days of maturation: alite (A); belite (B); brownmillerite (C); tricalcium aluminate (D); gypsum (G); anhydrite (H); calcium sulfate (S); calcite (K); portlandite (P); chalcopyrite (L)*

*Table 10. Phase composition of pozzolanic mortars made on the basis of XRD (Rietveld Refinement)*

| Phase | Chemical formula | Percentage of phases | | | | | |
|---|---|---|---|---|---|---|---|
| | | CEM I | CEM I + PFW | CEM II/B-V | CEM II/B-V + PFW | CEM III/A | CEM III/A + PFW |
| Alite | $3CaO \cdot SiO_2$ | 3.6 | 2.1 | 5.4 | 3.9 | 4.9 | 4.2 |
| β-Belite | $2CaO \cdot SiO_2$ | 5.1 | 1.6 | 8.1 | 6.5 | 8.5 | 13.0 |
| Brownmillerite | $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| Tricalcium aluminate | $3CaO \cdot Al_2O_3$ | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| Cordierite | $Mg_2Al_4Si_5O_{18}$ | 6.0 | 3.7 | 5.6 | 2.0 | 5.5 | 3.2 |
| Portlandite | $Ca(OH)_2$ | 18.2 | 10.4 | 17.7 | 13.9 | 18.5 | 12.5 |
| Ettringit | $Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 26H_2O$ | 4.3 | 1.7 | 0.9 | 2.5 | 0.8 | 2.4 |
| CSH | $CaO \cdot SiO_2 \cdot H_2O$ | 62.8 | 58.6 | 62.3 | 51.4 | 61.8 | 51.2 |
| CuCSH | $CaCu(SiO_4) \cdot H_2O$ | - | 7.6 | - | 9.0 | - | 3.0 |
| ZnCSH | $CaZn(SiO_4) \cdot (H_2O)$ | - | 14.3 | - | 10.8 | - | 10.5 |

The XRD data presented in Table 10 shows that cement mortars without post-flotation waste after 90 days contain the remains of unreacted clinker phases and products of the hydration process. The addition of copper post-flotation waste to cement for 25% of its mass, after 90 days of the hydration process, causes the appearance of silicates in the structure of the analyzed samples. Visible silicates contain in their structure ions: magnesium (Mg); iron (Fe) and aluminum (Al).

After 90 days of hydration, unreacted clinker phases were detected in all mortars: alite and belite, and additionally were not detected the fastest reacting phases - brownmillerite and tricalcium aluminate. An increase in the CSH phase content generates a decrease in the portlandite content. The active molecules were released and reacted with portlandite upon dissolution of the PFW particles, causing the $Ca(OH)_2$ to be partially consumed. The higher content of the CSH phase (without heavy metals) increases the compressive strength after 90 days of hardening. Moreover, CSH phases with embedded heavy metals: copper and zinc were detected in PFW mortars. The content of the CSH phase with the zinc ion is higher because zinc has a higher reactivity in an alkaline environment (pH of mortars above 10). The test results (XRD) indicate the formation of compounds with the participation of heavy metals, including their incorporation in the structure of the prepared cement composite.

## 4. Conclusions

The preliminary tests of the physicochemical and mineral properties of the cement mortars enhanced by PFW confirm that there are possibilities to recycle this kind of waste in the building materials. The performed investigations proved that the cooper post-flotation waste is a unique material with the potential to be used in construction materials. In these studies, the PFW was partly replacing cement (up 5 to 40% by mass) in cement mortars. The main conclusions are:

- The content of oxides forming the C-S-H phase is above 85% (the sum of the content of the three oxides (SiO2+ Al2O3+ Fe2O3).

- Copper ore post-flotation waste has a large BET surface area, the largest pore volume, and the lowest value of a loss on ignition compared to cement used in this research.
- These parameters increase the water demand for cement pastes. At a temperature of 20°C, the addition of up to 20% PFW delays the initial setting time by a maximum of 39%.
- Pozzolanic activity performed by EN 450-1 shows the highest value (77.7% after 28 days and 79.3% after 90 days) with cement containing a minimum of 95% Portland clinker. Cements with mineral additives, such as silica fly ash and granulated blast furnace slag, are characterized by lower pozzolanic activity with the addition of PFW compared to cement without additives. However, CEM II/B-V after 90 days of curing reached as much as 79.1% of the strength of the control mortar.
- The addition of 25% PFW reduces the compressive strength of mortar samples. However, the compressive strength of the composite made of CEM I (without mineral additives) is higher than the reference samples made of cements with mineral additives.
- The reduced temperature delays the initial setting time, drops the hydration reaction, and decreases the compressive strength.
- X-ray studies have shown that heavy metals are incorporated into the structure of the composite.

The performed studies confirmed the highest use of post-flotation waste in cement composites produced with Portland cement. In the case of composite Portland cement and blast furnace slag cement, the addition of PFW causes deterioration of the standard consistency, extension of setting time, and loss of a smaller amount of CSH phase, which reduces pozzolanic activity. Summarizing, Preliminary studies proved that PFW might be used in the building materials industry as an additive to cement composites. In addition, the new possibility of managing post-flotation waste may diminish the negative impact of this waste on the natural environment. In the future, the use of post-flotation waste may also reduce the consumption of cements, which production is expensive and energy consuming.

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