scientific reports

OPEN

Experimental study of the effect of seawater and temperature on the corrosion resistance of cement composites with the addition of copper post-flotation waste

Szymon Kalisz[1]✉, Elżbieta Haustein[2] & Marek Lieder[1]

The presented results of the study concern the determination of corrosion resistance of cement composites with the copper post-flotation waste (PFW) as a cement substitute in the amounts of 2.5%, 5.0%, 7.5%, and 10%, exposed to seawater, depending on the temperature (10°C and 20°C). To better evaluate and understand the compressive strength, the hydration products of the cement composites were analyzed after exposure to seawater at 28 and 360 days by TGA and XRD methods. The cement composites incorporating test material exhibited corrosion resistance in seawater, with samples containing 5 wt% PFW achieved the highest compressive strength of 69.7 MPa (at 20°C) and 68.9 MPa (at 10°C) after 360 days of immersion in seawater. The obtained results were higher by 27.9% and 3.6% compared to the control samples. The tests (360 days) showed the possibility of using copper as a post-flotation waste additive in up to 5% of cement mass without significant changes to cement composites' mechanical and chemical properties. The research results indicate the potential possibility of waste used in construction, which would not only allow for a significant reduction in the production costs of cement, including a reduction in CO_2 emissions, but above all, would eliminate the risk of its negative impact on the natural environment.

Keywords Copper post-flotation waste, Cement, Seawater, Compressive strength, Resistance coefficient, Temperature

The construction is the largest emitter of greenhouse gases, accounting for 37% of global emissions. For example, the production of Portland cement alone, a fundamental concrete component, is responsible for about 8% of global CO_2 emissions worldwide, necessitating the adoption of alternative cementitious binders to meet carbon neutrality goals[1].The adverse effects of global warming, among other things, include rising sea levels. Their growth may consequently increase the exposure of hydrotechnical objects to seawater attack, causing a decrease in their structural durability[2]. Seawater, mineral salts, and other components are significant in this process. Its composition depends on the geographical location. The analysis by[3] indicated that at an ambient temperature of 25 °C, the density of seawater is approximately 1.025 g/cm^3. The pH estimation is between 7.5 and 8.4, and the average value when it balances with CO_2 in the atmosphere is 8.2 [4,5]. In turn, the salinity of seawater, depending on the region marine, can range from 0.6 to 4.8%, with the generally accepted average salinity of 3.5%. For example, the salinity of the North Sea is 3.3%, the Red Sea is 4%, and the Baltic Sea is only 0.7% [4,6]. According to source[7] the construction objects are often subjected to the effects of carbonation and chemical processes resulting from the presence of chloride and sulfate ions, the content of which can be 46.6–77.5% (Cl^-) and 4.9–19.1% (SO_4^{2-}) of the total salts content dissolved in seawater. Additionally, they are exposed to cyclical wetting and drying of their surfaces depending on atmospheric conditions, including the impact of changing temperatures and microorganisms. The temperature has a significant effect on seawater penetration. For example, the diffusivity of chloride can increase by 23.5–41.6% when the temperature changes from 29 to 34 °C[8]. Temperature change causes an increase in the diffusion kinetics and a faster molecular speed of chloride ion transport into the structure. The

[1]Department of Process Engineering and Chemical Technology, Faculty of Chemistry, Gdansk University of Technology, Narutowicza 11/12, 80-233 Gdańsk, Poland. [2]Department of Mechanics of Materials and Structures, Faculty of Civil and Environmental Engineering, Gdansk University of Technology, Narutowicza 11/12, 80-233 Gdańsk, Poland. ✉email: szymon.kalisz@pg.edu.pl

mechanism of fluid and ion flow during the interaction of corrosive environments on the surface of construction buildings is the result of capillary suction (1), resulting from capillary action inside the capillaries of the mineral binder; permeation (2), resulting from pressure gradients; diffusion (3), resulting from concentration gradients; and migration (4), resulting from electrical potential gradients[9]. Corrosion resistance to seawater depends on the composition of the mineral binder, including mineral additives. The main components of the hydration reaction of Portland cement are amorphous calcium silicate hydrate (C-S-H phase), calcium hydroxide (portlandite) - CH, aluminates, ettringite, and unhydrated residues of clinker phases, etc[10]. The chemical stability of the resulting reaction products influences concrete's durability in aggressive environments[11]. As a result of the influence of seawater, ion chloride can be incorporated in calcium chloro-aluminate hydrates attached to calcium-silicate hydrate, blocking pores in concrete structures[12]. In turn, sulphate ions can react with cement hydration products to produce gypsum and ettringite, which can damage the mineral binder and increase chloride penetration into the structure, reducing the durability of concrete[13,14]. However, as the authors suggest[7], the high chloride content of seawater can suppress ettringite formation.

The unfavorable phenomenon of global warming forces the search for innovative solutions, including a new approach to using raw materials for cement production. There is a visible increase in interest in waste from the industrial economy. An example is post-flotation waste, by-products, from mining. The growing demand for copper and related products makes the processing of ores inevitable. This generates large amounts of waste, the leading solution of which is environmental disposal. The chemical and mineralogical composition of post-flotation waste is variable and depends on the type of processed ore. Preliminary research results indicate that post-flotation waste (PFW) can be used in materials buildings, e.g., cement mortars[15–18], concrete[17,19–21], and ceramic products[22]. For example, adding flotation waste to ceramic products reduces their shrinkage and water absorption. According to Kudełko (2018)[23], flotation waste can be used as a source of iron compounds to produce a hydraulic binder, i.e., Portland cement. They can be a primary or secondary cement component, a cement setting regulator, or an alternative fuel for producing Portland and aluminum cement. Literature sources state[24–29] that flotation waste improves the tightness and porosity of concretes; on the other hand, it causes a decrease in their mechanical strength and frost resistance.

The presented paper focuses on changes in properties related to the durability of cement composites after exposure to a seawater environment, depending on the temperature. Reference samples and samples with the tested material were analyzed using thermogravimetric analysis (TGA) and X-ray diffraction (XRD) to determine the effect of seawater on the type of phases resulting from the influence of the corrosive environment. The presented results constitute a pilot study on alternative waste materials that may constitute a new source for sustainable construction development, including practical and efficient management of waste accumulated in the environment. This study, by demonstrating the potential use of copper post-flotation waste as an additive in cement composites, may offer a promising solution to reduce the environmental impact of cement production.

Materials and experimental investigation

Ordinary Portland cement (class 42.5 R, Company Górażdże Poland) was used for this study. River sand obtained from the Borowiec Aggregate Exploitation Plant (Poland) with a specific gravity of 2.65 g/cm^3 was used as fine aggregate and tap water. All materials complied with the standards EN 197-1, EN 12,620, and EN 1008 [30–32]. The tested material was taken from the "Żelazny Most" tailings storage facility, owned by KGHM Polish Copper Inc. According to the European Waste Catalog[33], this type of waste is classified under code 01 03 81 and includes waste from flotation enrichment of non-ferrous metal ores other than those mentioned in 01 03 80. Figure 1; Table 1 show the microscopic (SEM) appearance of the grains and the chemical and physical properties of the tested material. The mean particle diameter of the test materials used in this study is 161. 7 µm (for waste) and 21.6 µm (for OPC 42.5R), respectively. The content of grains with a size of the tested waste in the total mass below 18 µm and the range from 18 to 150 µm, 150–250 µm, 250–600 µm is 5.2%, 41.7%, 38.5%, and 14.6%, respectively. Cement particles below 18 µm are 56.08%, 18–30 µm is 18.75%, 30–52 µm is 17.67% and 52–120 is 7.5%. The tested waste (PFW) grains are irregular, whereas the larger particle size shows a deformed surface with open-air pores. The non-uniform shape of the grains is a result of the copper ore processing process. In the previous publication[34], the authors presented detailed characteristics of selected chemical and physical properties of this waste, which is the research subject.

Cube samples (with sides 50 × 50 × 50 mm) were prepared using standard mortar mixing machines. The copper post-flotation waste was used as a replacement for cement up to 10% by weight, and the samples' composition details are presented in Table 2. A constant water-binder ratio was 0.45. The superplasticizer was added to obtain the solid consistency of fresh mortar mixtures.

Specimens were prepared and hardened for 24 h in steel moulds, and their surfaces were covered with foil. The prepared samples were divided into two series: matured at 10 °C (series no. 1.) and 20 °C (series no.2). All were placed in water. After 28 days, these series were divided into two more - one remained in water (series no.3), and the other was placed in a corrosive environment (series no.4), remaining at the temperatures assigned to them. For corrosive environments, these were a zero time to expose. Samples were placed in a curing chamber, where a constant temperature was ensured by a system receiving a signal from a temperature sensor placed in the water or seawater. The chemical composition of the seawater was as follows: NaCl – 30 g, $MgCl_2 \times 6H_2O$ – 6 g; $MgSO_4 \times 7H_2O$ – 5 g; $CaSO_4 \times 2H_2O$ – 1.5 g and $KHCO_3$ – 0.2 g in 1000 g H_2O (which corresponds to the average salinity: 33‰) — the samples' exposure time ranged from 28 to 360 days. The phase composition was studied using the XRD, and the portlandite content was determined by the method (TG-DTG) on cement composites without and with 2.5% (min.) and 10% (max.) of tested material (PFW) after 28 and 360 days of storage in the control and aggressive environments[35].

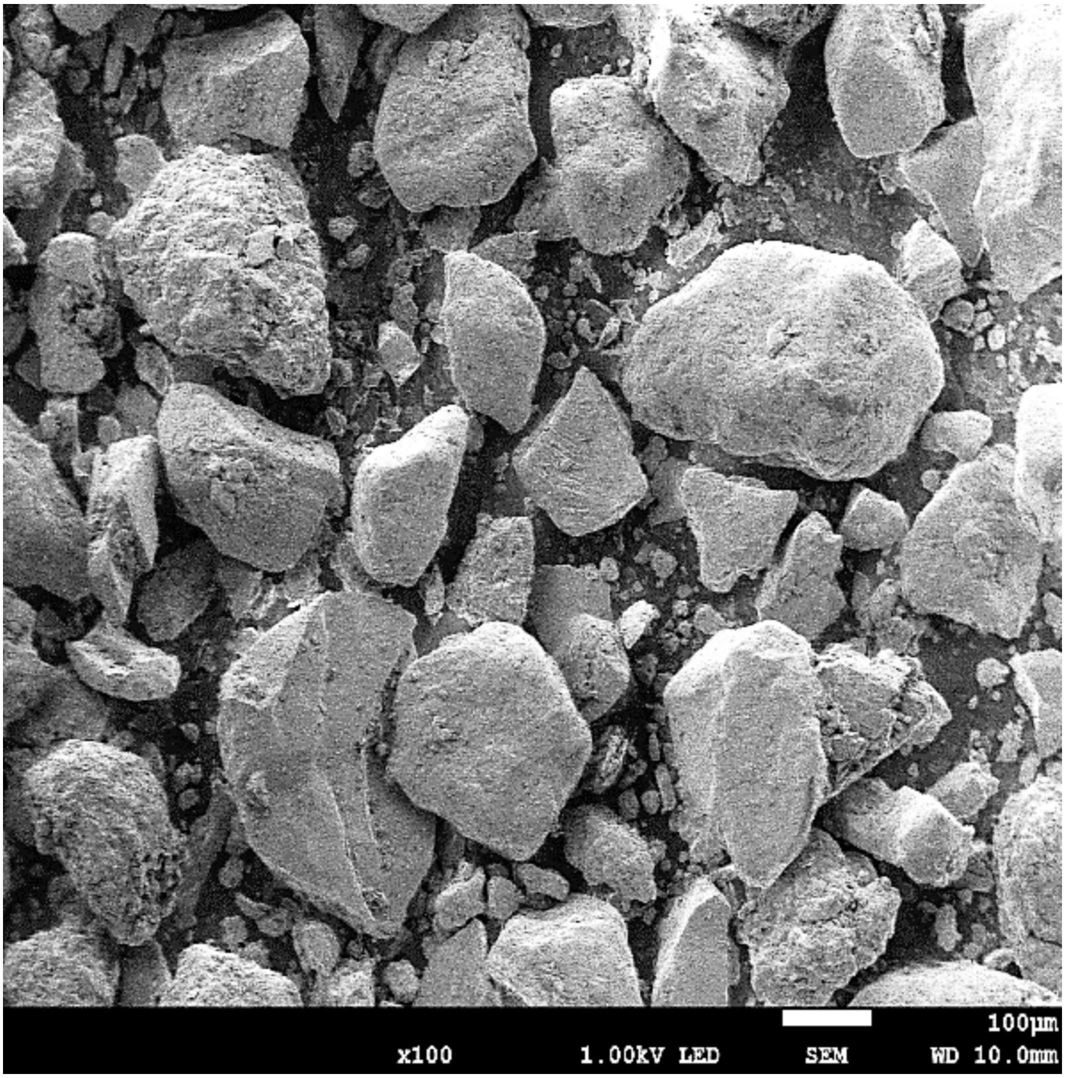


Fig. 1. SEM. Structure grains of the copper post-flotation waste (PFW), magnification × 100

Chemical composition		Physical properties	
Type of oxide form	**Content, wt%**		**Content, wt%**
CaO	19.0	Specific gravity, g/cm^3	2.7
SiO_2	61.6	Mean particle size, µm	161.7
Al_2O_3	5.6	BET surface area, m^2/g	3.0
Fe_2O_3	2.0	Total volume pore, mm^3/g	1.5
MgO	2.9	LOI	1.1
SO_3	3.1	pH	7.3
Na_2O_e*	1.9		
Heavy metals**	1.2		
Other	1.9		

Table 1. Composition of the cement composites without and with post-flotation waste (PFW), w/b = 0.45. *Na_2O_{eq} = %Na_2O + 0.658 · %K_2O; **Heavy metals – sum of CuO + ZnO + PbO + Co_3O_4

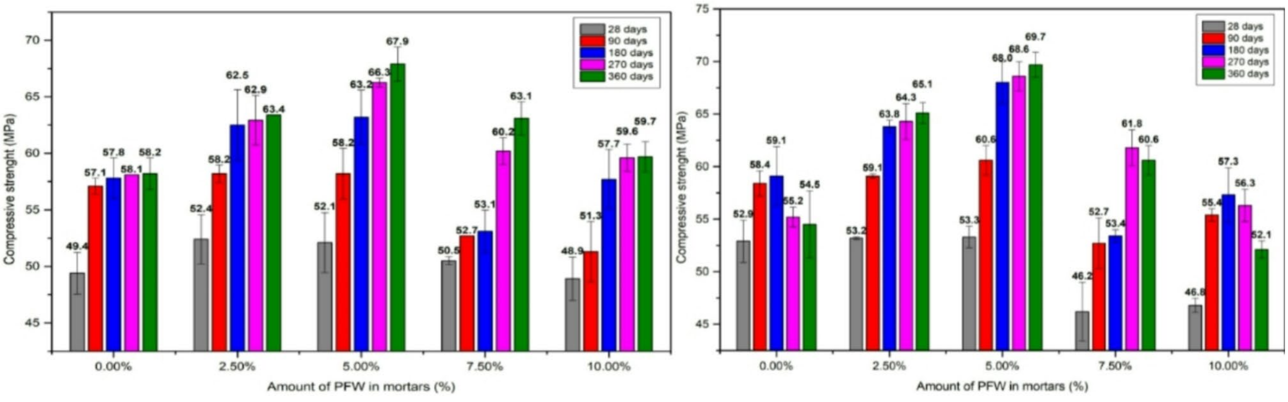
Results and discussion

Compressive strength of cement composites—temperature 10°C and 20°C

Figures 2 and 3 show the average compressive strength of cement composites without and with 2.5%, 5%, 7.5%, and 10% PFW in the water and seawater (3.3%) environments after exposure for 28, 90, 180, 270, and 360 days

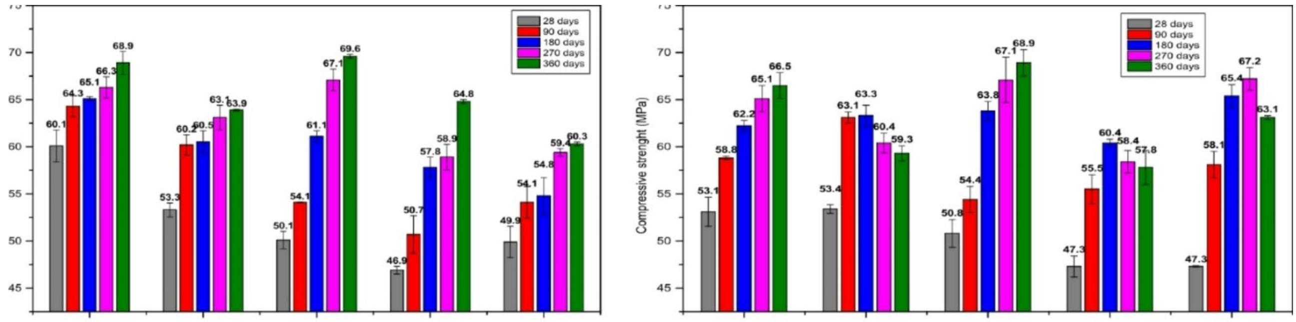
	Content of copper post-flotation waste (PFW), % wt.				
Type of composites	0.0	2.5	5.0	7.5	10.0
Waste (PFW), g	0.0	9.8	19.5	29.3	39.0
Cement (OPC 42.5 R), g	390.0	380.2	370.5	360.7	351.0
Fine aggregate - sand, g	1143.0	1143.0	1143.0	1143.0	1143.0
Water, g	173.5	173.5	173.5	173.5	173.5
Chemical admixture, g	2.0	3.9	3.8	3.5	3.4

Table 2. Composition of the cement composites without and with post-flotation waste (PFW), w/b = 0.45.



(a) (b)

Fig. 2. The average compressive strength of the cement composites without and with 2.5%, 5%, 7.5%, and 10% PFW after 28 to 360 days of curing in (**a**) water (control) and (**b**) corrosive environment (seawater) at 20°C.



(a) (b)

Fig. 3. The average compressive strength of the cement composites without and with 2.5%, 5%, 7.5%, and 10% PFW after 28 to 360 days of curing in (**a**) water (control) and (**b**) corrosive environment (seawater) at 10°C.

for two temperatures (20°C and 10°C).

The most significant increase in strength between 28 and 90 days of curing was achieved in the control sample and samples with the addition of 2.5% and 5.0% PFW. The recorded increase was 16% (for the control sample), 11% (for 2.5% PFW), and 12% for 5% PFW. In turn, the highest increase in strength (by 30%) between 28 and 360 days of curing was achieved by the sample containing 5.0% PFW. After 270 and 360 days of curing, higher compressive strength values of samples containing copper post-flotation waste in amounts from 2.5 to 10% were recorded compared to the PFW control sample (Fig. 2a). After 360 days of storage in a water environment, the values were higher by 8.2% (for 2.5%), 14.3% (for 5%), 7.8% (for 7.5%), and 2.5% for 10% PFW, respectively, compared to the value obtained for the sample without the research material. Taking into account the temperature (20°C), the observed increase in compressive strength for samples after 360 days compared to the values obtained after 28 days of curing stored in the water environment was: 17.8% (for 0%), 21.0% (for 2.5%), 30.3% (for 5%), 25% (for 7.5%) and 22.1% (for 10% PFW), respectively.

The data presented in Fig. 2b indicate that, in the reference sample, compressive strength decreases after 270 days of curing in seawater. There is a visible decrease in compressive strength development resulting from the penetration of chloride ions into the structure of samples. In turn, adding copper post-flotation waste in the amount of 2.5% and 5% of the cement mass causes an increase in the compressive strength value of the samples throughout the research period. These samples obtained the highest strength results: 65.1 MPa (2.5% PFW) and 69.7 MPa (5.0% PFW) after 360 days of storage in a seawater environment. The share of 7.5% PFW in the cement composite resulted in an increase in strength (by 33.8%) after 270 days compared to 28 days of curing. Further exposure to seawater (360 days) decreased compressive strength (7.5%) compared to 270 days. The observed increase in the total value for the research samples (after 360 days compared to 28 days at 20°C) was 2.9% (for 0%), 22.4% (for 2.5%), 30.8% (5%), 31.2% (for 7.5%) and 11.3% for 10% PFW. In turn, the mechanical strength of the PFW samples after 360 days of storage in seawater was higher by 19.4% (for 2.5%), 27.9% (for 5%), 11.2% (for 7.5%), and lower by 4.4% (for 10%) compared to the value obtained for the control sample stored in the same corrosive environment. The presented data indicate that the share of 2.5% and 5% PFW limits the penetration of chloride ions into the structure compared to the control mortar for the test period (360 days), including changes in phase composition, which influences the development of strength in a seawater environment at 20°C.

The data presented in Fig. 3 indicate that the environment's temperature impacts compressive strength development. In both environments (control and seawater), higher values were obtained for samples stored at 10°C than those stored at 20°C. For example, as shown in Fig. 3a, the average value of samples without and with PFW stored in a water environment after 360 days ranged from 60.3 MPa to 69.6 MPa (for 10°C) and from 58.2 MPa to 67.9 MPa for 20°C. In turn, the values for samples stored in a seawater environment after the entire research period ranged from 57.8 MPa to 68.9 MPa (for 10°C) and from 52.1 MPa to 69.7 MPa (for 20°C). The presented data indicate that exposure of the test samples at a temperature of 10°C allows for an increase in compressive strength after 360 days in comparison to the values obtained after 28 days of curing by, respectively: 14.7% (for 0%), 19.9% (for 2.5%), 38.9% (for 5%), 38.2% (for 7.5%), 20.8% for 10% PFW in a water environment and 25.2% (for 0%), 11% (2.5%), 35.6% (for 5%) 22.2% (for 7.5%) and 33.4% for 10% PFW in a seawater environment. The presented data indicate that the decrease in temperature slows down the bond hydration process, including the penetration, dissolution, and crystallization of corrosion products in the structure of the tested cement composites, without and with the participation of the tested research material. The decrease in compressive strength is visible with the increase in the involvement of the research material compared to the control environment. The highest compressive strength values were obtained for composite samples with 5% PFW, for which no decrease in value was observed throughout the entire test period. The higher compressive strength could be attributed to the formation of hydration products with lower crystal size and better packing in the structure of the tested composites after 360 days of exposure to seawater. A decrease in the strength (by 7.2%, 10.3%, and 5.1%) of samples with the addition of 2.5% and 7.5% (after 270 days) and 10% PFW (after 360 days) was observed after stored in a seawater environment at a temperature (10°C) compared to the values obtained for control samples, Fig. 3b. In summary, copper post-flotation waste positively affects cement mortars' compressive strength, especially up to 5.0%by mass cement. Their content increases resistance to a corrosive environment—attack by chloride ions from seawater and at low temperatures.

Corrosion resistance factor

Table 3 presents the results of the corrosion resistance coefficient of cement mortars without and with the tested material exposed to seawater, depending on the temperature (20°C and 10°C). The values shown are expressed as the ratio of the compressive strength in the corrosive environment (seawater) to the control environment (water) depending on the time exposure of cement composites (t).

The results of cement mortars' corrosion resistance coefficient tests - without and with the participation of the tested material - show their varied susceptibility to corrosion aggression depending on the temperature. Exposure (360 days) in the seawater environment changes the corrosion resistance coefficient of samples with PFW about the control samples, Table 3. These results suggest that cement composites with the addition of 2.5% and 5.0% copper post-flotation waste were characterized by higher resistance to seawater attack for 360 days. In turn, the increase in the content in amounts of 7.5% and 10% of the cement mass in the samples, including the porosity of the grain structure of the tested material and the occurring hydration reactions, have an impact on the decrease in corrosion resistance as a function of the time of exposure to the corrosive environment at 20°C. After 360 days at 20°C, the corrosion factor values for the cement mortar with the addition of 2.5%, 5.0%, and 7.5% PFW increased by 0.98%, 0.97%, and 4.3% compared to the initial corrosion resistance (28

	Days of curing in a seawater environment									
	28	90	180	270	360	28	90	180	270	360
Content of PFW, %	20°C					10°C				
0.0	1.07	1.02	1.02	0.95	0.94	0.88	0.91	0.96	0.98	0.97
2.5	1.02	1.02	1.02	1.02	1.03	1.00	1.05	1.05	0.96	0.93
5.0	1.02	1.04	1.08	1.04	1.03	1.01	1.01	1.04	1.00	0.99
7.5	0.92	1.00	1.01	1.03	0.96	1.01	1.09	1.04	0.99	0.89
10.0	0.96	1.08	0.99	0.94	0.87	0.95	1.07	1.19	1.13	1.05

Table 3. Corrosion resistance coefficient of cement composites without and with PFW (from 0 to 10%) stored in seawater environment depending on the temperature.

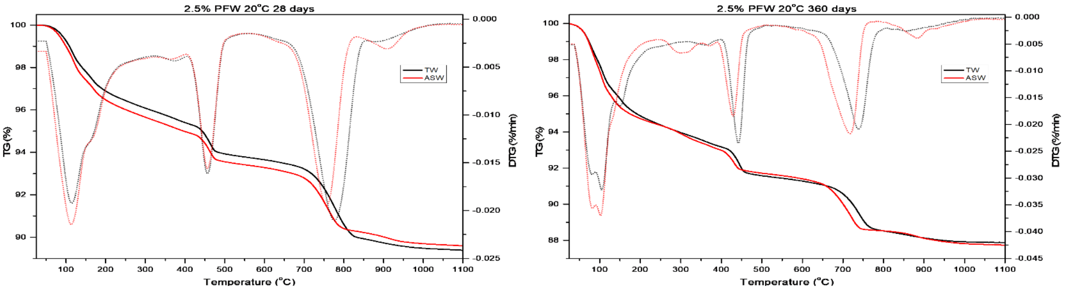


Fig. 4. TGA-DTG curves of the cement composites with 2.5% of the tested material after cured of 28 and 360 days at 20°C in the following environments: TW—tap water and ASW—seawater.

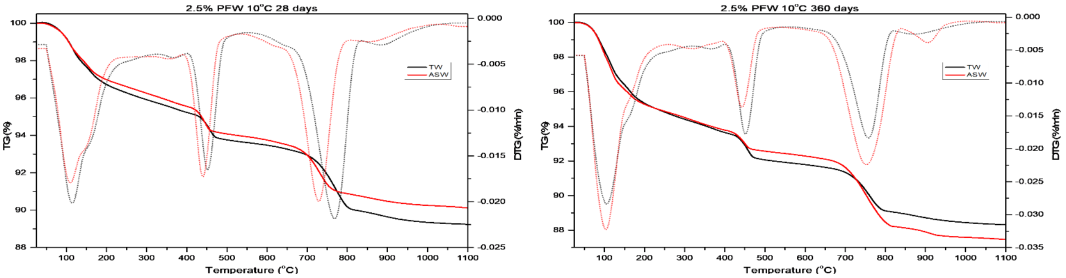


Fig. 5. TGA-DTG curves of the cement composites with 2.5% of the tested material after cured of 28 and 360 days at 10°C in the following environments: TW—tap water and ASW—seawater.

days). The change in the temperature of seawater exposure slows the formation of hydration bonding products with the tested material, including corrosion reaction products. For example, a visible decrease in the corrosion resistance value for the samples with the addition of tested material (from 2.5 to 10%) was noted after 270 days (at 10°C) compared to the value at 20°C.

The resulting expansive chemical compounds are conducive to reducing the porosity of cement composites in the initial period by slowly filling the free spaces with chloride corrosion products. This causes an increase in compressive strength followed by a decrease. Also, the angular sharp edges of copper post-flotation waste particles can improve the cohesion of the cement matrix in the first days of curing in corrosive environments. On the other hand, the glassy surface texture of tested material particles hurts the cement matrix's cohesion due to the corrosive environment. This results in the formation of internal voids and capillary channels in the cement mortars, causing a reduction in durability. Therefore, the strength of samples with lower copper post-flotation waste content is improved due to the positive effect of the tested material. However, if its content exceeds 7.5%, the corrosion resistance decreases. Heavy metals, such as zinc and copper, contained in copper post-flotation waste, as a result of chemical reactions, are probably incorporated into the crystalline phase CSH and ettringite, which reduces the compressive strength.

Analysis TGA, XRD

The hydration products are the main factor affecting the mechanical strength, including the corrosion resistance of samples. The content of the hydration product of the cementitious composites was characterized by analyzing the content of the $Ca(OH)_2$. The TGA/DTG curves for the cement composites with 2.5% (min.) and 10% PFW (max.) content after 28 and 360-day storage in the tap water (TW) and aggressive seawater (ASW) for two temperatures are shown in Figs. 4, 5, 6 and 7. The presented TGA/DTA curves show three weight loss zones.

Figures 4 and 5 show the distribution of exothermic peaks of samples containing 2.5% PFW stored in a controlled environment and seawater after 28 and 360 days at 20°C and 10°C, respectively. Considering exposure time, type of environment, and temperature conditions, the size of the exothermic peaks varies significantly. The amount of C-S-H gel has changed due to the kind of additive introduced. Hence, the intensity of the exothermic peak associated with the mass loss from the decomposition of C-S-H gel increased at later ages (12 months), as seen in DTA thermograms. The dehydroxylation of portlandite is responsible for the endothermic peak in the 395–450 °C range. Due to the pozzolanic activity of the tested material, the peak of portlandite after exposure for 28 days at both temperatures is more intense than that of peaks after 360 days.

Figures 6 and 7 illustrate the DTA thermograms of the sample with 10% PFW stored in both environments after 28 and 360 days at 20°C and 10°C. The endothermic effects shown are noticeably more minor, indicating a slow pozzolanic reaction caused by the increase in test material. It is observed that the mass loss from the hydration of ettringite increased in samples, which can be due to the presence of sulphate in the seawater compared to the storage period of 28 days. The mass loss due to the dehydroxylation of CH and decarbonization was relatively lower, which is attributed to the slow carbonation of CH due to carbonate ions or binding with free chloride ions.

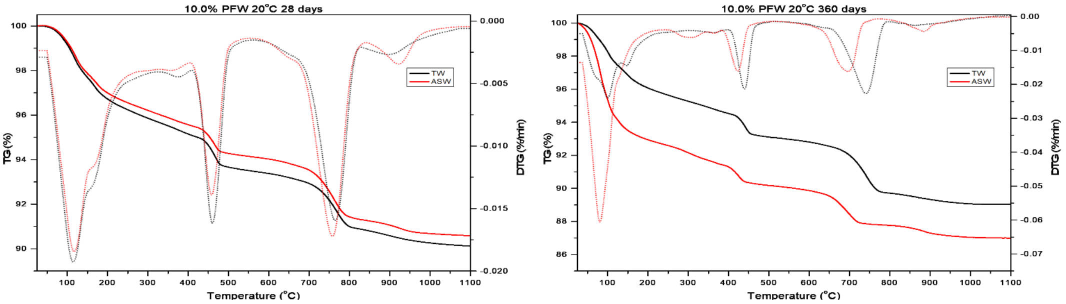


Fig. 6. TGA-DTG curves of the cement composites with 10% of the tested material after cured of 28 and 360 days at 20°C in the following environments: TW—tap water and ASW—seawater.

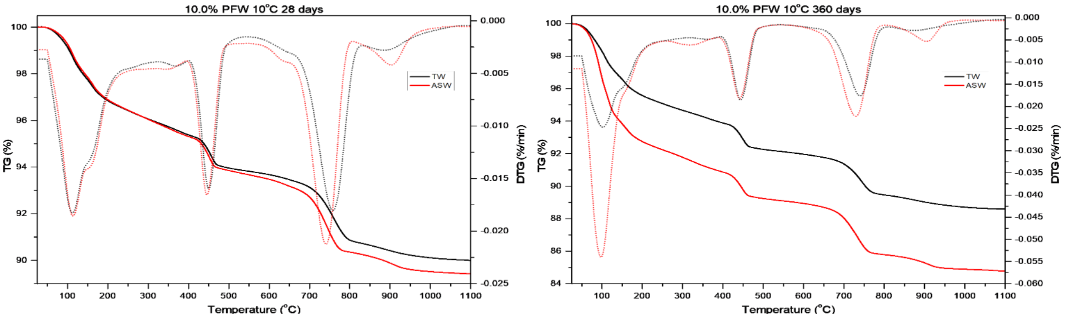


Fig. 7. TGA-DTG curves of the cement composites with 10% of the tested material after cured of 28 and 360 days at 10°CC in the following environments: TW—tap water and ASW—seawater.

Exothermic peaks of samples stored in water for 360 days can be observed, shifting towards temperatures with increasing hydration age. This change occurs with less weight loss. This loss of masse decreases proportionally as the substitution rate of the addition increases. The endothermic effect in the 50–400 °C temperature range is related to the loss of water chemically bound in calcium aluminosilicate hydrates and calcium sulfo-aluminate hydrates (e.g., ettringite and mono-sulfate). As the immersion time increased, the amounts of hydration products increased with the disappearance of $Ca(OH)_2$. This was also due to the continuous reaction of ions chloride with $Ca(OH)_2$. Endothermic peaks due to carbonation were also detected. Then, the intensity and the sharpness of the exothermic peaks decreased. In the DTG curves presented of the samples stored in the seawater, they observed two new mass loss humps (~ 310 and 910 °C), which are attributed to the formation of Friedel salt (FS, $C_4ACl_2H_{10}$) and sodium sulfate, respectively.

The calcium hydroxide ($Ca(OH)_2$) content is one of the leading indices of cement hydration degree. The thermogravimetric method was used to determine the content of copper post-flotation waste-modified cement composites accurately. According to the TG-DTG curves, the $Ca(OH)_2$ contents in the hardened samples were calculated for the addition of 0%, 2.5% (min.), and 10% (max.) PFW after exposure in control and corrosive environments after 28 and 360 days, depending on the temperatures, as shown in Tables 4 and 5. The calcium hydroxide ($mCa(OH)_2$) content was determined using the Equation:

$$Ca(OH)_2 \underset{\rightarrow}{T} CaO + H_2O \qquad CaCO_3 \underset{\rightarrow}{T} CaO + CO_2$$

$$\begin{aligned} Ca(OH)_{2\ (measured)} = {} & \frac{M\ Ca(OH)_2}{M\ H_2O} \cdot weightloss\ Ca(OH)_2 \\ & + \frac{M\ CaCO_3}{M\ CO_2} \cdot weightloss\ CaCO_3 = 4.11 \cdot weightloss\ Ca(OH)_2 \\ & + 2.27 \cdot weightloss\ CaCO_3\ \frac{74.09}{18.02} \cdot weightloss\ Ca(OH)_2 \\ & + \frac{100.09}{44.01} \cdot weightloss\ CaCO_3 \end{aligned}$$

In the case of tested waste, the calculated hydroxide content may not reflect the actual value, as the additive's bulk density is much lower than Ordinary Portland Cement; therefore, the same material mass occupies a much larger volume. In addition, during the thermal decomposition of copper post-floatation waste, water may be present in its grains, affecting the test results.

		Type of environments			
		Tap Water		Seawater (3.3%NaCl)	
Content PFW	Type of chemical compound	28	360	28	360
0.0%	Ca(OH)$_2$, %	1.63	2.12	1.88	1.87
	CaCO$_3$, %	4.04	3.22	3.07	3.62
	Portlandite content, %	15.87	16.02	14.70	15.90
2.5%	Ca(OH)$_2$, %	1.49	1.9	1.53	1.6
	CaCO$_3$, %	3.36	2.74	2.79	2.81
	Portlandite content, %	13.75	14.03	12.62	12.95
10.0%	Ca(OH)$_2$, %	1.73	1.69	1.19	1.41
	CaCO$_3$, %	2.57	2.98	2.31	2.04
	Portlandite content, %	12.94	13.71	10.13	10.43

Table 4. Content of portlandite (wt%) in the cement composites without and with 2.5% and 10% PFW in control and corrosive environments after 28 and 360 days at 20°C.

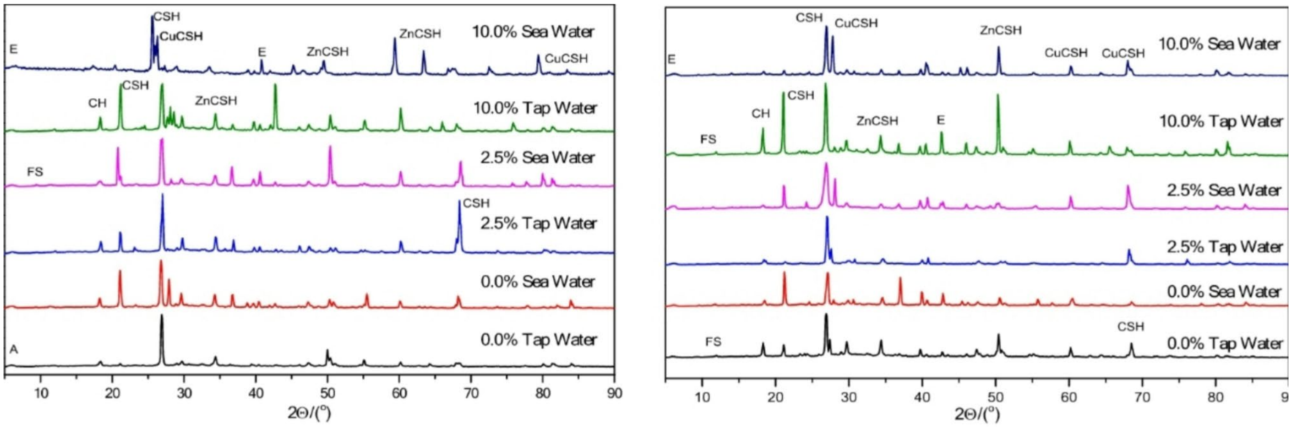
		Type of environments			
		Tap Water		Seawater (3.3%NaCl)	
Content PFW	Type of chemical compound	28	360	28	360
0.0%	Ca(OH)$_2$	1.66	2.15	1.64	1.79
	CaCO$_3$	2.17	3.10	2.68	2.80
	Portlandite content	11.75	15.87	12.82	13.71
2.5%	Ca(OH)$_2$	1.69	1.87	1.64	1.40
	CaCO$_3$	3.46	2.74	2.85	3.92
	Portlandite content	14.80	13.91	13.21	14.65
10.0%	Ca(OH)$_2$	1.64	1.90	1.62	1.83
	CaCO$_3$	2.88	1.89	3.08	3.02
	Portlandite content	13.28	12.10	13.65	14.38

Table 5. Content of portlandite (wt%) in the cement composites without and with 2.5% and 10% PFW in control and corrosive environments after 28 and 360 days at 10°C.

The endothermic effect observed in the TG curves (Figs. 6 and 7) in the 450–550 °C temperature range, with a maximum at approx. 500 °C, is attributed to the weight loss associated with Ca(OH)$_2$ dehydroxylation. In tested composites, calcium hydroxide occurs as crystalline portlandite but can also have an amorphous form. The data presented in Table 4 indicate the increasing content of calcium hydroxide in the tested composites, where its content depends on the amount of added waste and the time of exposure in the control and seawater environment. The reaction processes in the tested samples without and with copper post-floatation waste stored in both environments affect the content of products in the mineral binder. The data presented in Table 4 indicate the increasing content of calcium hydroxide in the tested composites, where its content depends on the amount of added waste and the time of exposure in the control and seawater environment. The reaction processes in the tested samples without and with copper post-floatation waste stored in both environments affect the content of products in the mineral binder. For example, the exposure after 28 days in a seawater environment of samples with tested material resulted in a decrease in portlandite content by 8.2% for 2.5% PFW and by 21.7% for 10% PFW compared to the content of this product in samples stored in the control environment. After 360 days, the portlandite content decreased by 0.75% (for the control sample), 7.7% for the sample with 2.5% PFW, and 23.9% for the sample with 10% PFW, respectively.

The data presented in Table 5 indicate that the change in storage temperature in the control and corrosive environment affects the portlandite content in the tested samples. The decrease in temperature slows down the crystallization of the hydration reaction products of the control samples after 28 and 360 days of storage in both environments. The addition of the research material causes an increase in the Ca(OH)$_2$ content by 5.1% (for 2.5% PFW) and 15.9% for 10% PFW after 360 days of storage in the seawater environment compared to its content in the samples stored in the water environment.

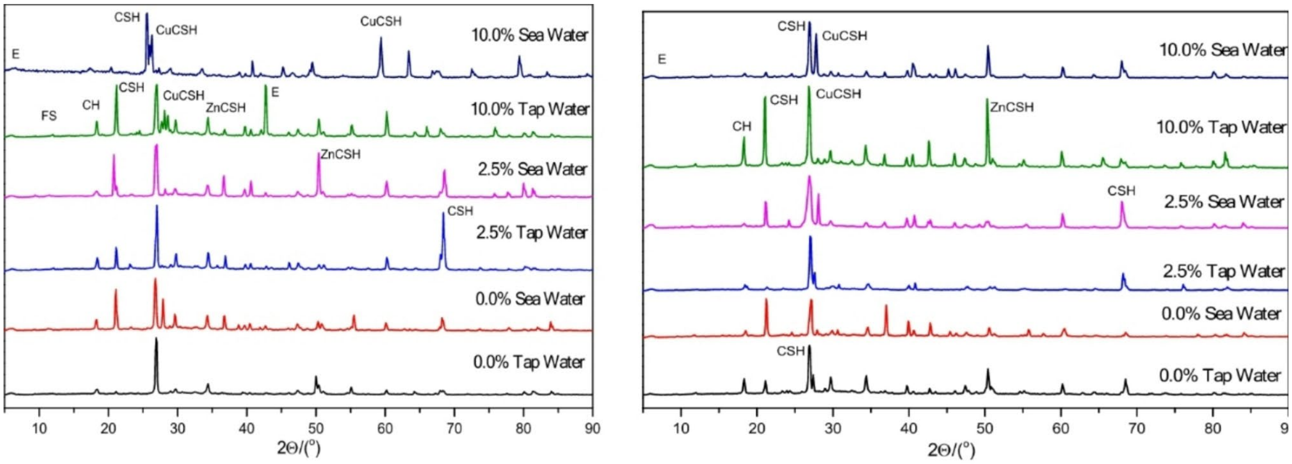
Replacing part of the cement with an addition slows the hydration reaction. It may dilute the cement's clinker part with a concomitant aluminate and reduce calcium silicate content. In turn, a drop in temperature affects the crystallization process of the resulting reaction products.



(a)

(b)

Fig. 8. XRD pattern of cement composite without and with 2.5% and 10.0% of PFW after (**a**) 28 days and (**b**) 360 days of exposure in tap water and artificial seawater at 20°C.



(a)

(b)

Fig. 9. XRD pattern of cement composite without and with 2.5% and 10.0% of PFW after (**a**) 28 days and (**b**) 360 days of exposure to tap water and artificial seawater at 10°C.

Phase composites

XRD patterns were recorded after exposure to seawater and the control environment of cement composites without and with 2.5% and 10% PFW for 28 and 360 days to determine the compounds formed in the samples for two temperatures. The results are shown in Figs. 8 and 9.

The hydration of OPC involves the conversion of tri-calcium silicate (C_3S) into calcium silicate hydrate (C-S-H) and calcium hydroxide (CH). C-S-H is the main binder that contributes to strength, whereas CH is a secondary hydration product that typically has low phase stability in aggressive environments. The chemical interactions of these components in seawater with waste could reduce hydrate stability and cause hydrate leaching, compromising long-term material durability. The phase composition XRD tests of the specimens with 2.5%and 10% PFW stored in tap water at 20°C after 28 and 360 days indicated the presence of CSH phase, portlandite, calcium aluminosilicates, and ettringite (Figs. 8 and 9). In all figures, the characteristic peaks of CH were observed at positions 18.08°. Although the peak intensity of CH was not directly proportional to the content of CH in hardened samples, the content of CH could be viewed as an indicative description of the variations with the test material. It was noticed that the peak intensities of CH at around 18.04° presented a slight decrease as the content of PFW increased. The peak intensity was usually related to the content of the corresponding mineral phase. This result showed that adding copper post-flotation waste caused a minor delay in cement's hydration process and reduced CH formation. Visible reflections at approx. 29° and 49° confirm the presence of hydrated calcium silicate phases with zinc or copper ions in the specimens. Reflections at 28°, 31°,

Environment	Type of sample/time of hydration		Chemical formula/Name of phase	Unreacted clinker phases	Portlandite	CSH	Ettringite	Dolomite	Zn-CSH	Cu-CSH
				–	$Ca(OH)_2$	$CaO·SiO_2·H_2O$	$Ca_6Al_2(SO_4)_3(OH)_{12}·26H_2O$	$CaMg(CO_3)_2$	$CaZn(SiO_4)·H_2O$	$CaCu(SiO_4)·H_2O$
Water	100% OPC	28	% by weight of the total mass	15.1	17.7	62.7	1.4	3.1	–	–
		360		12.3	18.2	64.8	1.9	2.8	–	–
	2.5% PFW	28		7.3	16.7	58.4	2.1	2.9	9.2	3.4
		360		5.6	17.1	57.5	1.1	3.4	10.6	4.7
	10.0% PFW	28		8.9	16.1	56.3	2.3	2.5	9.0	4.9
		360		4.4	16.8	58.0	2.2	2.6	10.2	5.8
Artificial Sea Water	100% OPC	28		11.2	14.2	68.4	2.9	3.3	–	–
		360		8.3	16.9	70.0	2.2	2.6	–	–
	2.5% PFW	28		9.4	14.6	54.8	2.1	2.7	10.5	5.9
		360		8.1	15.3	51.1	3.3	3.0	12.2	7.0
	10.0% PFW	28		7.4	14.1	57.9	1.7	2.6	10.9	5.4
		360		6.7	14.4	55.4	2.2	2.0	11.9	7.4

Table 6. Phase composition content in cement composites after exposure (28 and 360 days) in control (water) and aggressive seawater at 20°C.

Environment	Type of sample/time of hydration		Chemical formula/Name of phase	Unreacted clinker phases	Portlandite	CSH	Ettringite	Dolomite	Zn-CSH	Cu-CSH
				–	$Ca(OH)_2$	$CaO·SiO_2·H_2O$	$Ca_6Al_2(SO_4)_3(OH)_{12}·26H_2O$	$CaMg(CO_3)_2$	$CaZn(SiO_4)·H_2O$	$CaCu(SiO_4)·H_2O$
Water	100% OPC	28	% by weight of the total mass	27.6	12.8	56.7	2.0	0.9	–	–
		360		14.6	14.2	68.8	1.3	1.1	–	–
	2.5% PFW	28		35	16.4	29.7	1.2	2.8	10.3	4.6
		360		6.4	15.5	57.7	0.2	2.7	11.2	6.3
	10.0% PFW	28		24.6	14.4	35.3	1.8	2.2	13.6	5.1
		360		16.3	13.2	40.4	1.0	2.4	18	8.7
Artificial Sea Water	100% OPC	28		26.7	12.8	58.6	1.1	0.8	–	–
		360		14.1	13.2	70.3	1.9	0.5	–	–
	2.5% PFW	28		31.4	15.7	35.3	1.9	2.6	10.8	2.3
		360		23.2	14.7	41.6	0.8	2.1	12.8	4.8
	10.0% PFW	28		28.5	14.4	33.4	2.3	2.4	13.3	5.7
		360		5.8	13.3	51.5	1.3	2.0	16.4	9.7

Table 7. Phase composition content in cement composites after exposure (28 and 360 days) in control (water) and aggressive solutions at 10°C.

and 43° confirm the presence of ettringite in the specimens and are more intensive in the control sample with 2.5% PFW at 20°C after 28 days compared to the intensity of these reflections after 360 days.

Tables 6 and 7 present the phase analysis results of mortar samples without and with the addition of 2.5% (min.) and 10% (max.) PFW after 28 and 360 days of exposure in the control environment and seawater stored at 20°C and 10°C, respectively.

The data presented in Table 6 shows that exposure of test samples with PFW to the seawater environment at a temperature of 20°C reduces the content of unreacted clinker phases in the cement composites. For example, after exposure to seawater (360 days), the unreacted clinker phase content for the sample with 10% PFW was 6.7% compared to the control sample (8.3%). Considering the main hydration products CSH and $Ca(OH)_2$ phase, a decrease in their content in the samples is visible from 2.5% to 10% PFW compared to the control sample, regardless of the type of environment used.

Hydrated calcium silicates - CSH phase is produced by the reaction between the amorphous glassy silica present in pozzolan and CH made due to the hydration of cement. The presence of this hydration reaction product affects the durability of concrete, cement mortars, and cement composites exposed to aggressive corrosive environments. Using copper post-floatation waste as a cement substitute in the tested composites impacts the decrease in the hydration component $Ca(OH)_2$ content. Additionally, the particles of the research material fill the spaces between the cement particles as the hydration time passes, thickening the structure of the research samples and strengthening the interfacial area. The share of PFW in the amount of 10% of the cement mass after 360 days of storage in corrosive environments causes a decrease in the dolomite content compared to the sample stored in water. As suggested by Souza et al.[36], one of the possible explanations for dolomite consumption can be the "dolomitization" process caused by ion exchange between the Ca^{2+}, Mg^{2+}, and CO_3^{2-}

Content of tested material, %	Type of environment	Ratio	
		ET/CSH*)	ET/CH*)
0% PFW	water	0.0293	0.1044
	seawater	0.0314	0.1302
2.5% PFW	water	0.0191	0.0643
	seawater	0.0646	0.2157
10.0% PFW	water	0.0379	0.1310
	seawater	0.0397	0.1528

Table 8. The ratio of ET/CSH and ET/CH of the cement mortar without and with 2.5% (min.) and 10% (max.) of the tested material after 360 days at 20°C, depending on the type of environment. *) ET – ettringite; CSH – calcium silicate hydrate, CH – portlandite.

Content of tested material, %	Type of environment	Ratio	
		ET/CSH*)	ET/CH*)
0% PFW	water	0.0189	0.0915
	seawater	0.0270	0.1439
2.5% PFW	water	0.0035	0.0129
	seawater	0.0192	0.0544
10.0% PFW	water	0.0248	0.0758
	seawater	0.0252	0.0977

Table 9. The ratio of ET/CSH and ET/CH of the cement mortar without and with 2.5% (min.) and 10% (max.) of the tested material after 360 days at 10°C, depending on the type of environment. *) ET – ettringite; CSH – calcium silicate hydrate, CH – portlandite.

ions in the solid phase and alkali ions (i.e., Na^+) in the pore solution, as the occurrence in alkali- carbonate reaction. In turn, heavy metals in copper and zinc in the copper post-floatation waste are incorporated into the structure of hydrated calcium silicates due to the hydration of Ordinary Portland Cement. The data in Table 5 show that the interaction of chloride ions after 360 days impacts the decrease in faze CSH with Zn and Cu.

The change in the temperature of both environments (water and seawater) impacts the process of shaping the content of individual mineral phases in the tested composites, depending on the exposure time. Considering the temperature (20°C), a higher content of, for example, the CSH phase and $Ca(OH)_2$ was noted in the cement composite without and with the participation of the research material for both environments compared to the temperature of 10°C. The temperature drop affects the mineral binder's dissolution and crystallization of chemical compounds. For example, exposure at a temperature of 10°C causes a decrease in the CSH phase content by 9.6%, 49.1%, and 37.3%, respectively, for the control sample and samples with the addition of 2.5% and 10% PFW compared to the content for the temperature of 20°C after 28 days of exposure in the water environment. In turn, exposure to a seawater environment at a temperature of 10°C caused a decrease in the CSH phase content for samples with 2.5% and 10% PFW by 35.6% and 42.3% (after 28 days) and 18.6% and 7.0% after 360 days, respectively, compared to the content for a temperature of 20°C.

The portlandite content results agree with the data obtained from XRD analysis. The differences result from the determination methodology and the course of many reactions simultaneously, especially in the case of thermal analysis (TGA).

Tables 8 and 9 show the ratio (ET/CSH and ET/CH) of the leading products of cement mortar hydration processes without and with the addition of 2.5% (min.) and 10% (max.) of the tested material after 360 days of curing at 20°C and 10°C, depending on the type of environment.

The test results presented in Table 8 indicate that the ratio of ettringite to CSH and CH for the samples stored in seawater to the control environment (water) after 360 days was 6.7% and 19.8% (for the control sample), 70.4% and 70.2% (for 2.5% PFW), and 4.5% and 14.3% for 10% PFW higher, respectively. The highest value of the ettringite to portlandite ratio after 360 days of storage in the seawater environment was found for the cement composite with the addition of 2.5% PFW (0.2157). At the same time, the tested sample showed the highest compressive strength value – 65.1 MPa (Fig. 6), and the highest corrosion resistance coefficient – 1.03 (Table 3) for this research period. The lowest ratio value (ET/CH) was obtained for the control sample – 0.1044, whose compressive strength and corrosion resistance coefficient were 54.5 MPa and 0.94, respectively. A similar relationship was noted for the tested samples exposed to seawater. The obtained values indicate that the higher the ET/CSH and ET/CH ratio, the higher the corrosion resistance.

The effect of lower temperature (10°C) influences the ratio of ettringite content to CSH phase and CH content. The values presented in Table 9 are lower than those obtained for samples stored at 20°C (Table 8). For example, the ratio (ET/CSH) values for samples exposed to a corrosive environment at 10°C are lower than 20°C by 14.0%, 70.3%, and 36.5%, respectively. A similar relationship was observed for the ratio (ET/CH). The effect of lower temperature slows down the corrosion processes occurring in the structure of the tested composites between the individual components. Considering the seawater environment, the results of the studies indicate that Cl – ions diffused into the structure of the samples both at room temperature and at low temperature because of its relatively high diffusion coefficient. The observed effect (XRD and TG/DTG studies) is the formation of Friedel's salt. After Friedel salt was formed from monosulfate by substituting Cl^- ions, SO_4^{2-} ions were released into the solution in the pores, which favors the simultaneous formation of ettringite in the tested samples. The data presented in Tables 8 and 9 suggest that the ET/CSH and ET/CH ratios correlate well with the obtained compressive strengths, corrosion resistance coefficient, and chemical composition depending on the type of corrosive environment and the amount of test material as a cement substitute in cement composites.

The presented research results indicate that the chemical composition of the waste under study, depending on the temperature, impacts the behavior of cement composites exposed to seawater. The phase changes occurring in the samples also impact the mechanical strength, including corrosion resistance. Considering the data obtained, replacing the cement mass with less reactive waste has affected the course of the mineral binder's hydration reaction. The irregular copper waste particles increase the cement matrix's cohesion over extended curing periods. Their use increases the bonding of the cement composite with its other components. Compressive strength development is gradually dominated by the pozzolanic reaction with curing time, resulting in a sharp increase in the strength values at later ages for the cement composites with 2.5% and 5.0% PFW. The mechanism of the impact of the tested waste may result from its impact as a filler (physical effect), where PFW fills the intergranular spaces between cement particles and sand. Their chemical composition due to the reaction with cement (chemical effect) forms a denser mineral binder matrix by creating crystallization sites for cement particles, thus becoming part of the binder matrix, which affects mechanical strength development. In turn, seawater exposure time causes active chloride ions to settle in free spaces and react with the surface, forming salts, which increase their volume, filling the free spaces in the structure of mortar samples and causing a change in their properties. A decrease in the solubility of portlandite in a corrosive environment involving the tested material limits the diffusion of ions from seawater into cement composites.

Summary

Seawater attacks negatively affect the development of expansive products, salt crystallization, and hydrate dissolution. It also has beneficial effects like pore structure densification and hydration acceleration. The dominance of positive or negative effects determines the seawater's impact on cementitious materials' durability. Analyzing the test results of cement composites with a copper post-flotation waste (PFW), which were exposed to a seawater solution in two temperatures (20°C and 10°C) for 360 days, the following conclusions can be drawn:

- The highest compressive strength value, after 360 days of seawater exposure, was noted for the sample with 5% PFW. The value increased by 19.8% (20°C) and 18.4% (10°C) compared to the samples stored in the control environment.
- The share of 10% PFW after 360 days of exposure to a corrosive environment at 20°C causes a decrease of 10.5%, and at 10°C causes an increase of 8.4% in the compressive strength value compared to the control sample.
- The highest values (1.08 and 1.19) of the corrosion resistance coefficient were obtained for the sample with 5% PFW (at 20°C) and 10% PFW (at 10°C) after 180 days of exposure to seawater. After this period, a decrease in corrosion resistance was noted, resulting from the reactions occurring in the tested cement composites.
- The expansive chemical compounds contribute to reducing the porosity of cement composites in the initial period of exposure to a corrosive environment by slowly filling the free spaces with chloride corrosion products. This causes an increase in compressive strength followed by a decrease.
- The change in storage temperature in the control and corrosive environment affects the portlandite content in the tested samples. The decrease in temperature slows down the crystallization of the hydration reaction products of the control samples after 28 and 360 days of storage in both environments. XRD and TG/DTG tests confirm the observed phenomenon.
- The tested waste in the initial phase of mineral binder binding acts as a filler (physical effect) of free inter-granular spaces, and then, as a result of chemical changes, its chemical composition affects the chemical reactions that occur in the structure of the tested samples.
- Chlorides from seawater reacting with tri-calcium silicate (C_3A) and/or gypsum ($CaSO_4$) consume the formed portlandite (CH) in the cement hydration process, resulting in the formation of products such as ettringite or Friedel salts.

The presented data indicate that post-flotation waste can be a new source of mineral additives in the construction industry, maintaining its optimal share without significantly impacting the decrease in mechanical strength. The results of this investigation are not only significant but also promising. They show that cement composites containing copper post-flotation waste are corrosion-resistant to seawater. These results highlight the potential of this type of waste, thus inspiring further research in the development of materials engineering. Among the presented tests, the most distinguished sample was the one with 5% PFW, which the authors consider the most beneficial and optimal additive to the cement composite to obtain the best corrosion resistance without affecting the composite's compressive strength and performance parameters.

Data availability

The datasets used and analysed during the current study available from the corresponding author on reasonable request.

Received: 30 November 2024; Accepted: 11 March 2025

References

1. Barbhuiya, S., Bhusan Das, B. & Adak, D. Roadmap to a net-zero carbon cement sector: Strategies, innovations and policy imperatives. *J. Environ. Manage.* **359**, 121052 (2024).
2. Ting, M. Z. Y. & Yi, Y. Durability of cementitious materials in seawater environment: A review on chemical interactions, hardened-state properties and environmental factors. *Constr. Build. Mater.* **367**, 130224 (2023).
3. Millero, F. J. & Huang, F. The density of seawater as a function of salinity (5 to 70 g kg − 1) and temperature (273.15 to 363.15 K). *Ocean. Sci.* **5**, 91–100 (2009).
4. Li, P., Li, W., Sun, Z., Shen, L. & Sheng, D. Development of sustainable concrete incorporating seawater: A critical review on cement hydration, microstructure and mechanical strength. *Cem. Concr Compos.* **121**, 104100 (2021).
5. Saxena, S. & Baghban, M. H. Developments in the built environment seawater concrete: A critical review and future prospects. *Dev. Built Environ.* **16**, 100257 (2023).
6. Weerdt, K., De, Bernard, E., Kunther, W., Thostrup, M. & Lothenbach, B. Cement and concrete research phase changes in cementitious materials exposed to saline solutions. *Cem. Concr Res.* **165**, 107071 (2023).
7. Yi, Y., Zhu, D., Guo, S., Zhang, Z. & Shi, C. A review on the deterioration and approaches to enhance the durability of concrete in the marine environment. *Cem. Concr Compos.* **113**, 103695 (2020).
8. Farahani, A., Taghaddos, H. & Shekarchi, M. Prediction of long-term chloride diffusion in silica fume concrete in a marine environment. *Cem. Concr Compos.* **59**, 10–17 (2015).
9. John, E. & Lothenbach, B. Cement hydration mechanisms through time – a review. *J. Mater. Sci.* **58**, 9805–9833 (2023).
10. Lavagna, L. & Nistic, R. Applied sciences an insight into the chemistry of cement — A review. (2023).
11. Beaudoin, J. J., Catinaud, S. & Marchand, J. Volume stability of calcium hydroxide in aggressive solutions. **31**, 149–151 (2001).
12. Lambert, P. C., Page, C. & Short, N. Pore solution chemistry of the hydrated system tricalcium silicate/sodium chloride/water. *Cem. Concr Res.* **15**, 675–680 (1985).
13. Yu, L., Chu, H., Zhu, Z., Jiang, L. & Dong, H. Determination of the chloride ion content in concrete under simultaneous chloride and sulphate ion attack. *J. Build. Eng.* **72**, 106579 (2023).
14. Heikal, M. et al. Prolonging the durability of maritime constructions through a sustainable and salt-resistant cement composite. (2023).
15. Kalisz, S., Kibort, K., Mioduska, J., Lieder, M. & Małachowska, A. Waste management in the mining industry of metals ores, coal, oil and natural gas - A review. *J. Environ. Manage.* **304**, 114239 (2022).
16. Rosado, S., Gullón, L., Martínez, L. F. M. & Llamas Borrajo, J. F. Potential uses of copper wastes in the Building sector: inertization and added value solutions. **25** (2021). https://doi.org/10.3390/materproc2021005025
17. Onuaguluchi, O. & Eren, Ö. Cement mixtures containing copper tailings as an additive: Durability properties. *Mater. Res.* **15**, 1029–1036 (2012).
18. Gou, M., Zhou, L. & Then, N. W. Y. Utilization of tailings in cement and concrete: A review. *Sci. Eng. Compos. Mater.* **26**, 449–464 (2019).
19. Saedi, A., Jamshidi-Zanjani, A. & Darban, A. K. A review on different methods of activating tailings to improve their cementitious property as cemented paste and reusability. *J. Environ. Manage.* **270**, 110881 (2020).
20. Muleya, F. et al. Investigating the suitability and cost-benefit of copper tailings as partial replacement of sand in concrete in Zambia: an exploratory study. *J. Eng. Des. Technol.* https://doi.org/10.1108/JEDT-05-2020-0186 (2020).
21. Thomas, B. S., Damare, A. & Gupta, R. C. Strength and durability characteristics of copper tailing concrete. *Constr. Build. Mater.* **48**, 894–900 (2013).
22. Izak, P., Delikhovskyi, Y. & Olszyna, A. Use of Post-Flotation solidified tailings from copper production for ceramic tile production. *Mater. (Basel)* **16**, 1–12 (2023).
23. Kudełko, J. Effectiveness of mineral waste management. *Int. J. Min. Reclam. Environ.* **32**, 440–448 (2018).
24. Henne, A., Craw, D., Vasconcelos, P. & Southam, G. Bioleaching of waste material from the Salobo mine, Brazil: Recovery of refractory copper from Cu hosted in silicate minerals. *Chem. Geol.* **498**, 72–82 (2018).
25. Kotarska, I., Mizera, B. & Stefanek, P. Mining Waste in the Circular Economy - Idea Versus Reality. *E3S Web Conf.* 41, 1–7 (2018).
26. Lidelöw, S., Mácsik, J., Carabante, I. & Kumpiene, J. Leaching behaviour of copper slag, construction and demolition waste and crushed rock used in a full-scale road construction. *J. Environ. Manage.* **204**, 695–703 (2017).
27. Rossetti, P., Dino, G. A., Biglia, G. & Costa, E. Characterization of Secondary Raw Materials From Mine Waste: a Case Study From the Campello Monti Ni ± Cu ± Co ± Pge Mining Site (Western Alps, Italy). (2019).
28. Azevedo, A., Oliveira, H. A. & Rubio, J. Treatment and water reuse of lead-zinc sulphide ore mill wastewaters by high rate dissolved air flotation. *Min. Eng.* **127**, 114–121 (2018).
29. Muravyov, M. I., Fomchenko, N. V., Usoltsev, A. V., Vasilyev, E. A. & Kondrat'Eva, T. F. Leaching of copper and zinc from copper converter slag flotation tailings using H 2SO 4 and biologically generated Fe 2(SO 4) 3. *Hydrometallurgy* **119**, 40–46 (2012).
30. EN 197-1. Cement. Part 1: Composition, specifications and conformity for common cements, European Standards. (2012).
31. EN 12620. Aggregates for concrete. (2013).
32. EN 1008. 'Mixing water for concrete. Specification of sampling, testing and evaluation of the suitability of mixing water for concrete, including water recovered from production processes, European Standards' (2004).
33. SEPA. Guidance on using the European Catalogue (EWC) to code waste November 2015 Waste. 55. (2015).
34. Kalisz, S., Lieder, M. & Haustein, E. & Kuryłowicz-Cudowska, A. Sustainable utilization of copper post-flotation waste in cement composites. *Constr. Build. Mater.* **377**, (2023).
35. Santhanam, M. et al. RILEM TECHNICAL COMMITTEE RILEM TC-238 SCM recommendation on hydration stoppage by solvent exchange for the study of hydrate assemblages. **5**, (2018).
36. Souza, D. J., DE, Medeiros, M. H. F. & Hoppe Filho, J. Evaluation of external sulfate attack (Na2SO4 and MgSO4): Portland cement mortars containing fillers. *Rev. IBRACON Estruturas E Mater.* **13**, 644–655 (2020).

Author contributions

S.K:- principal researcher in the preparation of the article- preparation of the manuscript text- preparation of figures and tables- preparation of samples- performance of all compressive strength tests and chemical analysis- responses to reviewers. E.H.:- preparation of the manuscript text- substantive support in the field of civil engineering- assistance in making samples- language correction- responses to reviewers. M.L.:- supervisor of the work- substantive support in the field of chemistry.

Declarations

Competing interests
The authors declare no competing interests.

Additional information
Correspondence and requests for materials should be addressed to S.K.

Reprints and permissions information is available at www.nature.com/reprints.

Publisher's note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Open Access This article is licensed under a Creative Commons Attribution-NonCommercial-NoDerivatives 4.0 International License, which permits any non-commercial use, sharing, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if you modified the licensed material. You do not have permission under this licence to share adapted material derived from this article or parts of it. The images or other third party material in this article are included in the article's Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this licence, visit http://creativecommons.org/licenses/by-nc-nd/4.0/.

© The Author(s) 2025

MOST WIEDZY Downloaded from mostwiedzy.pl