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Assessment of the durability and environmental impact of seawater-activated portlandite-calcined clay binder

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This study investigated the performance of seawater-cured calcined clay-portlandite binder as a potential alternative to ordinary portland cement (OPC) for marine concrete applications. The samples for the investigation were prepared by mixing calcined kaolinite and bentonite clays in different ratios with portlandite. Seawater served as both the mixing and curing agent while acting as an activator due to its chloride and sulfate ion contents. The process involved three sequential steps: evaluating the changes in the mechanical performances, assessing the microstructural features, and estimating the environmental impacts. The results showed that the bound and total chloride content was significantly higher in the calcined clay mixes than in the OPC. The higher kaolinite enhanced the mechanical properties, and the strength-providing phases were Friedel's salt, C-A-S-H, ettringite, and zeolites. It was concluded that this novel binder has the potential to reduce global warming by 85–90% more than OPC.

Keywords: Calcined clays; seawater; Cl sequestration; durability; lifecycle analysis; marine concrete

1. Introduction

The ordinary portland cement (OPC) emits 5–8% of the world's CO₂ emissions [1] and is on an upward trajectory, as the current global cement production of approximately 4000 MT/year is expected to grow by 12–23% by 2050 [2]. Every kilogram of OPC emits almost 0.912 kg of CO₂ during production [3]. Its durability is also considered poor [4,5]; as the sulfate ions from seawater can cause cracks by forming ettringites, which may degrade the OPC concrete within a few months [6], reducing the service life of coastal structures. The use of potable water for mixing and curing concrete is also raising concerns due to the increasing scarcity of fresh water globally [7–10].

Ancient Roman concrete stands as a remarkable example of an extremely durable material that has endured exposure to seawater for over two millennia. It was produced using a mixture of seawater, volcanic ash, and slaked lime [11–14]. It offers a pathway to producing highly durable concrete with low environmental impacts [15,16], as the structures they built lasted for centuries; required much less energy to produce than modern OPC; and utilized seawater, which could mitigate our freshwater shortage [15,16]. Accordingly, in the past few years, several attempts have been made to develop novel cementitious materials by mimicking the ancient Roman concrete [16–18], but they were limited by the lack of raw materials such as coal fly ash and slag [19]. A previous study observed that combining calcined clay and portlandite with seawater can reproduce the microstructural phases of ancient Roman concrete while also providing reasonable compressive strength of around 17 MPa after 28 days of curing in seawater [20]. Seawater acts as an activator in

this system and leads to faster hydration and superior strength compared to other lime-pozzolan binders [20]. This binder system was named 'Recreated Roman Cement/Concrete' or 'RRC' [20].

The use of calcined clay and seawater to produce OPC concrete has been discussed in several studies. For example, in a series of studies, Liu et al. demonstrated that seawater, sea sand, limestone, and calcined clay improve concrete's mechanical performance and durability [21,22]. Zhang et al. reported that coupling limestone, calcined clay, and seawater with OPC enhances the concrete's mechanical properties [23], and other studies that employed limestone-calcined clay cement reported that it was less permeable and exhibited greater chloride binding capacity than OPC concrete [24,25].

This study primarily focuses on evaluating the durability as well as the environmental impacts of the RRC binder. Hence a life cycle analysis was conducted and compressive strength was considered a parameter for making RRC functionally equivalent to OPC. Since the binder is produced by combining calcined clay and seawater, it is expected to reduce both the carbon footprint and freshwater consumption of OPC. It should be noted that the hardening of the portlandite and calcined clay in the RRC binder relies on pozzolanic reactions in the presence of seawater [20] that result in microstructural characteristics that are different from those in OPC; therefore, the sulfate and chloride binding capacity of the RRC was measured to evaluate its durability in the presence of seawater.

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2. Experimental details

2.1. Materials and sample preparation

Bentonite and kaolinite clays deemed analytically pure were blended at different ratios to mimic natural clay deposits. Kaolinite clay converts to amorphous metakaolin by dehydroxylation at 700–850 °C [20,26,27]; however, metakaolin recrystallizes when calcined at a higher temperature [20,27], and bentonite needs to be calcined at 900 °C to achieve total amorphization [20,28]. The clay blends were therefore calcined at 750 °C to achieve total kaolinite and partial bentonite reactivity while avoiding recrystallization. The chemical compositions of kaolinite and bentonite clay were measured using X-ray fluorescence (XRF) and are shown in Table 1. The composition of the artificial seawater that was produced in the laboratory by mixing 680 g of sea salt (Instant Ocean) with 18.9 L of water is given in Table 2. Commercially purchased Portlandite was added at a 3:1 ratio of calcined clay to portlandite to activate the calcined clay's pozzolanic property; the mix proportions used are shown in Table 3. The ratio of water to cement for the calcined clay-based batches was 0.36, and the mixing water was composed of seawater and tap water in a proportion of 2:1, respectively, by mass. Sika Viscocrete-6100 was added as the superplasticizer, and river sand was used as a fine aggregate to fabricate the mortar. According to preliminary strength assessments, a low sand/binder ratio is required for calcined clay-based mortars; therefore, the sand-to-binder ratio of the clay mixes was fixed at 0.88. One OPC batch was also prepared to compare its microstructural properties and environmental footprint with the calcined clay binders. The OPC specimens' w/c and the sand/binder were respectively 0.45 and 2.75, and no superplasticizer was used. The higher w/c was used to enable the OPC to achieve compressive strength similar to that of the calcine clay-based batches.

Mortar samples were cast into 50 mm cubic molds to determine their compressive strength, and 25 mm × 25 mm × 250 mm mortar bars were prepared to determine changes in length. The binder and sand were dry mixed for 2 min in a Hobart mixer at the lowest speed (140 rpm), then seawater was added and mixed in for 30 s. The superplasticizer

was first mixed with tap water, then added to the mixture and mixed for another 30 s. The mixing speed was then gradually increased by mixing at a medium speed (285 rpm) for 30 s and then at the highest speed (580 rpm) until a homogenous consistency was achieved. The mixture procedure was completed in 5.5 to 6 min, then the mixture was poured into the cube and beam molds and sealed with plastic wrap. The specimens were demolded after 24 h and were submerged in seawater. Small paste disks were also prepared to measure the chloride and sulfate binding and analyze the microstructure.

2.2. Test procedures

2.2.1. X-ray diffraction analysis

X-ray diffraction (XRD) analysis was conducted at 3, 7, 14, 28, 56, and 90 days on a Bruker D-8 spectrometer, using Cu K α radiation (40 kV, 40 mA) [29]. The sample was scanned over a 5°–60° (2 θ) range, using a step size of 0.01 per second, and paste samples were pulverized to a particle size of <75 μ m and put on a holder.

2.2.2. Chemical extraction analysis

Salicylic acid-methanol (SAM) extraction was performed to calculate the percentage of insoluble residue in the initial mass of geopolymer gel and unreacted clay [30] by dissolving 1 g of the paste sample in a solution of 4 gm of salicylic acid and 60 ml of methanol [30]. The mixture was stirred for 2 h and filtered using a Whatman filter of 0.2 μ m pore size. Hydrochloric acid (HCl) extraction was performed by mixing 1 g of the ground paste sample with

Table 3. Mix proportions.

	Mixes				
	Calcined clay: portlandite = 3:1				
	Designation	Kaolin	Bentonite	w/c	Superplasticizer
RRC	75/25	75%	25%	0.36	5.15%
	50/50	50%	50%	0.36	5.15%
	25/75	25%	75%	0.36	5.15%
OPC				0.45	0

Table 1. Chemical composition (wt.%) of the raw materials.

Raw material	Mass fraction w/%							
	Al ₂ O ₃	SiO ₂	CaO	Fe ₂ O ₃	Na ₂ O	MgO	SO ₃	K ₂ O
Metakaolin	41.1	55.5	0.274	0.987	x ^a	0.0848	0.0515	0.145
Bentonite	18.7	68.4	1.5	4.25	3.09	2.39	0.881	0.420
OPC	3.87	21.2	65.3	3.10	x ^a	0.816	4.28	0.679

^ax-not detected.

Table 2. Chemical composition of artificial seawater.

Compositions	Na	Cl	S	Mg	Ca	K	Sr	Br	CO ₃
g/L	10.78	19.29	2.66	1.32	0.4	0.42	0.01	0.06	0.2

250 ml of HCl in a 1:20 volume ratio (ie 1 part 37 wt. % HCl and 20 parts H₂O) [30,31].

2.2.3. X-ray fluorescence (XRF) analysis

The chloride and sulfate binding properties of the mixes were measured by XRF analysis, using a Rigaku NEX CG spectrometer. (The instrument manual recommends using 4 g/4 ml of a sample for each analysis.) The paste disks were pulverized with a mortar pestle and passed through a #200 sieve as per ASTM E1621 [32]. Four (4) g of the fine powder were then pressed into pellets, using a pellet press, and the total chloride content was measured using XRF.

The determination of free chloride involves three sequential steps: extracting free chloride from cement paste into water according to ASTM C1218 [33], conducting an XRF analysis of the liquid sample, and proportionating the analyzed value to compare it with the total chloride content in 4 g of cement paste. According to ASTM C1218 and ASTM C114, the sample must be ground fine enough to pass through a #20 sieve to extract the chloride ions [33,34]. Important to note, the #200 sieve could not be used in this experiment because if the sample is too fine, excessive silica gel may form during nitric acid digestion and slow subsequent filtration [34]. It should also be noted that powder fineness up to 600 μ m has little effect on the extraction of water-soluble chloride [35,36]. The samples were prepared by mixing 10 mg of the powder with 50 ml of reagent water, covering the mixture with foil, then boiling it for 5 min and letting it cool for 24 h. Fine-textured Type II Class G filter paper was used to filter the liquid, then 3 ml of (1:1) nitric acid and 3 ml of hydrogen peroxide (30% solution) were added to the filtrate and the solution was boiled again for a few seconds. After it cooled down, the sample was stored in the refrigerator. Four (4) g of the liquid sample were analyzed to measure the free chloride content, and the bound chloride content was calculated by subtracting the free chloride content from the total chloride content in 4 g of cement paste.

XRF analysis is a simpler, less time intensive process than the traditional titration method for determining chloride content [37]. The samples were prepared precisely, the XRF analyses were performed with respect to the calibrated standards for solid and liquid samples, and the repeatability of the analysis was verified. (The method for calibrating the solid and liquid standards and the repeatability of the XRF analysis are presented in the [Supplementary Material](#) section).

2.2.4. Scanning electron microscope (SEM) analysis

The microstructure of the clay mixes was analyzed with a HITACHI 3000 N SEM scanning electron microscope. A mortar and pestle was used to break the paste sample into pieces, and one of the thin cracked pieces was attached to the holder with carbon tape and coated with gold-palladium. Secondary electron images were taken, keeping the accelerated voltage mostly at 20 kV, and a combination of a points analysis and an electron dispersive analysis (EDS) confirmed the formation of hydration products.

Polished samples were prepared for the SEM-EDS analysis by drying the samples in the oven at 40 °C for 48 h, then embedding them in a low-viscous epoxy formulated according to the supplier (Ted Pella) instructions. The epoxy-embedded sample was kept in a vacuum desiccator for 24 h to eliminate bubbles before being oven-dried at 65 °C for three days. The hardened epoxy-coated specimen was cut with a diamond-tipped saw to expose the specimen's cross-section, and the exposed surface was polished with polishing cloths ranging from 30 μ m to 0.25 μ m. The prepared samples were coated with gold-palladium before the analysis.

2.2.5. Evaluating the physical properties

The compressive strength of the mortar cubes was measured following the ASTM C109 method at 7, 28, and 90 days of curing, using an MTS Landmark Servo hydraulic test system with a loading rate of 200–400 lb/s [3,38]. The change in length of the mortar bars due to exposure to seawater was also measured, following the specifications of ASTM C157 [39]. This experiment was conducted to determine the volumetric expansion of clay-based mortar caused by the formation of reactive products binding different ions from the seawater. An early length expansion was observed, due to initial water absorption, but it stabilized after seven days; therefore, a zero reading was taken seven days after submerging the specimens to incorporate the effect of the ingress of seawater ions [6].

2.2.6. Environmental impact analysis

2.2.6.1. Goal and scope definition. This study evaluated the environmental performance of calcined clay-portlandite binders by conducting a life cycle analysis, using SimaPro 9.0.0.48. A cradle-to-gate approach was considered, which involves acquiring the raw materials, transporting them to the plant, and producing the concrete/mortar [40,41]. The Tool for the Reduction and Assessment of Chemical and Other Environmental Impacts (TRACI), developed by the U.S. Environmental Protection Agency, was used to assess the environmental impacts caused by the binders and mortars.

2.2.6.2. Functional unit. Most studies consider mass-based functional units [42,43], but since one unit mass of one binder is not functionally equivalent to one unit of another binder; therefore, other parameters, such as compressive strength and durability, must be considered when comparing the functionality of different binders. Some studies have considered the cement functional performance (CFP) as a functional unit since it takes into account the mass of the binder needed per cubic meter of mortar or concrete to achieve 1 MPa of compressive strength (kg/(m³.MPa)) [44,45]. The functional unit considered in this study was related to the CFP of the produced specimens, using various binder mixtures.

2.2.6.3. Lifecycle inventory. A superplasticizer was used in the clay-portlandite mortar to achieve adequate

Table 4. Material needed to achieve 1 MPa of compressive strength per m³ mortar.

Kaolinite to bentonite ratio (K/B)	28 days Compressive strength (MPa)	Cementitious binder (kg/MPa)	Superplasticizer, (kg/MPa)	Sand (kg/MPa)	Water (kg/MPa)
K/B = 75/25	29.57	33.49	1.72	29.47	10.33
K/B = 50/50	28.50	34.75	1.78	30.58	10.72
K/B = 25/75	22.90	43.25	2.22	38.05	13.34
OPC	50.03	11.07	0	30.45	4.98

Table 5. Energy required for processing per ton of clay.

Calcination of clay	Electricity	kWh	5
Grinding + packaging + other	Electricity	kWh	15

workability. The sand-to-binder ratio and w/c ratio were different in the OPC and the clay-based mortar; therefore, we calculated the quantity of these materials in proportion to the binder that were needed to achieve 1 MPa of compressive strength, and the results are shown in Table 4. The impacts caused by these materials were analyzed separately and combined to achieve the ultimate impact of mortar. The amount of binder used per m³ of mortar in the OPC and calcined clay-portlandite was 553.95 kg and 990.55 kg, respectively.

A temperature of 750 °C is needed to calcine and achieve reactivity of the kaolin and bentonite; however, the furnace used in this study for conducting calcination was not appropriate for industry standards. Therefore, the energy-required data for calcination was taken from the literature to predict the real-life environmental impacts shown in Table 5 [40,43].

The Cut-off, U classification of the Ecoinvent 3 dataset of SimaPro software was employed as the inventory for this study; to allocate the responsibility for environmental impacts caused by the production of materials on the primary users. Recyclable materials are cut off from the production activity [46]. In this research, SimaPro was used to consider the impacts caused by the manufacturing and gathering of raw materials for binder or mortar production, and Table 6 shows the categories of materials selected from the Ecoinvent 3 database for each material. The superplasticizer used in this study was sika viscocrete-6100, and its environmental impact per kg was obtained directly from the vendor. Table 7 shows the impact data for the superplasticizer.

2.2.6.4. Impact assessment methods. A variety of impact assessment methods are available that address normalization and characterization factors and impact assessment categories, but as mentioned earlier, the TRACI impact assessment method was employed in this study. TRACI includes the following impact categories: ozone depletion (kg CFC-11 eq), global warming (kg CO₂-eq), smog (kg O₃-eq), acidification (kg SO₂-eq), eutrophication (kg N-eq), carcinogenic (CTUh), non-carcinogenic (CTUh), respiratory effects (kg PM_{2.5}-eq), ecotoxicity (CTUe) and fossil fuel depletion (M.J. surplus). In

Table 6. Dataset used from Ecoinvent 3.

Input	Simapro material category
Ordinary Portland cement (OPC)	Cement, Portland (RoW) market for cut-off, U
Clay	Clay (CH) market for clay cut-off, U
Lime	Lime, packed (RoW) market for lime, packed cut-off, U
Water	Water, deionized, from tap water, at the user (RoW) market for water, deionized, from tap water, at user cut-off, U
Sand	Sand (GLO) market for cut-off, U
Electricity	Electricity, high voltage (U.S.) market group for cut-off, U

Table 7. Environmental impact per kg caused by the superplasticizer.

Impact category	Unit	Per kg superplasticiser
Ozone depletion	kg CFC-11 eq	2.30E-10
Global warming	kg CO ₂ eq	1.88E + 00
Smog	kg O ₃ eq	0
Acidification	kg SO ₂ eq	2.92E-03
Eutrophication	kg N eq	1.03E-03
Carcinogenic	CTUh	0.00E + 00
Non-carcinogenic	CTUh	0.00E + 00
Respiratory effects	kg PM _{2.5} eq	0.00E + 00
Ecotoxicity	CTUe	0.00E + 00
Fossil fuel depletion	M.J. surplus	2.91E + 01

addition, the US EPA considers environmental impacts with 100-year time horizons [47].

3. Results and discussions

3.1. Compressive strength

Figure 1 shows the compressive strength of the calcined clay mixes at 7, 28, and 90 days of curing with seawater. The 75/25 mix registered the highest compressive strength. The chloride ions in the seawater promoted the dissolution of clay and portlandite particles, and reacted with the aluminate in the clay to generate Friedel's salt, which enhanced the matrix densification. Ettringite formed as a result of the influx of sulfate ions through seawater curing; however it did not cause the volume expansion or eventual degradation of the concrete that it causes in the OPC system. The portlandite that is responsible for both the expansion and degradation in OPC system is consumed at an early age in the calcined clay mixes [6,48]

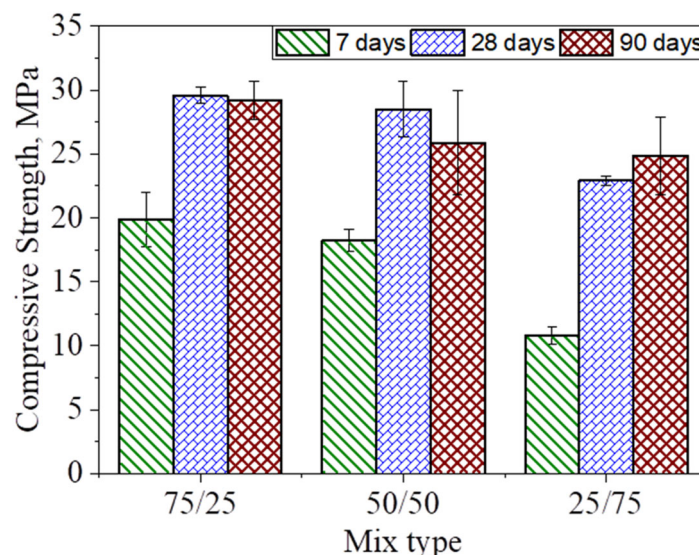


Figure 1. Compressive strengths of different calcined clay-portlandite batches with various kaolinite to bentonite (K/B) ratios.

(see Figure 2). Therefore, it can be concluded that calcined clay-portlandite mortars can achieve 25 to 30 MPa compressive strength within 28 days of construction and can be used as a substitute for traditional normal-strength concrete. Interestingly, within 28 days of the curing period, all the samples achieved more than 90% of the long-term strength that is normally achieved after 90 days. This leads to the conclusion that despite the portlandite-pozzolana binder system being characterized as slow-reacting, the presence of seawater can generate strength similar to that of traditional binders. This phenomenon matches previous findings that monitored the heat of reaction in the calcined clay-portlandite system with and without seawater [20].

Substituting calcined bentonite clay for calcined kaolin clay resulted in decreased compressive strength, as the coupled effect of a slower reaction rate and low aluminate content leads to lower compressive strength in mixes containing a 50% or higher amount of calcined bentonite clay. After 90 days of curing, the 25/75 batch (75% calcined bentonite) showed nearly 15% less strength than the 75/25 batch (25% calcined bentonite). A minimum of 25 MPa strength was achieved from all the batches after 90 days of curing, leading to the conclusion that medium-grade clay (~50% kaolinite) can be used to produce a calcined clay-portlandite binder system with reasonable strength (~25 MPa).

3.2. Durability assessment

3.2.1. Phase identification by X-ray diffraction analysis

Figure 2 shows the mineralogical formations caused by the reaction of RRC and OPC with seawater over time. Using seawater as the mixing and curing agent for the calcined clay-based binder is influential in forming certain phases, such as Friedel's salt, ettringite, and calcium aluminate monosulfate. Distinctive Friedel's salt peak was observed in all clay mixes at 11.4° after three days, primarily because the highly reactive alumina in calcined

kaolin speeds up the formation of AFm phases and eventually binds the chloride ions to form Friedel's salt (Cl-AFm) [49–51]. An increase in the peak intensity of Friedel's salt could be observed over time. The formation of ettringite was another vital phase detected in both RRC and OPC mixes due to sulfate ions in the seawater. In the OPC system, ettringite forms from a reaction between tricalcium aluminate hydrate and calcium sulfate [52]; in the RRC system, the highly reactive alumina captures sulfates from the seawater and forms ettringites with calcium ions provided by the portlandite. Friedel's salt and ettringites were observed in the XRD analysis of pure OPC mixed with seawater; nevertheless, the clay and OPC mixes showed a stark contrast in peak intensity, with the clay mixes recording a much higher peak intensity of the mineral formations. Worthy to note, Friedel's salt formation was higher in the calcined clay mixes compared to the OPC.

Portlandite was added to the RRC system as a calcium source to produce reaction products with binding properties. Figure 2(a–c) indicates that nearly all the portlandite in all the RRC mixes was consumed in seven days. In contrast, as shown in Figure 2(d), portlandite formed in the OPC mix's hydration process over time. Phillipsite, a type of zeolite that leads to a heterogeneous microstructure formation, is another critical phase that was observed in the calcined clay mixes [52]. However, a previous research suggested that the formation of phillipsite leads to lower mechanical performance [53].

3.2.2. Chloride binding capacity of RRC

3.2.2.1. *Quantification of chloride ions' binding capacity.* Three distinct categories of chloride ions are found in concrete: those chemically bound in Friedel's salt, physically bound in the diffuse layer of calcium alumina silicate hydrates (C-A-S-H), or present in the pore solution [36,54]. High alumina content in calcined clays increases the formation of tetra calcium aluminate

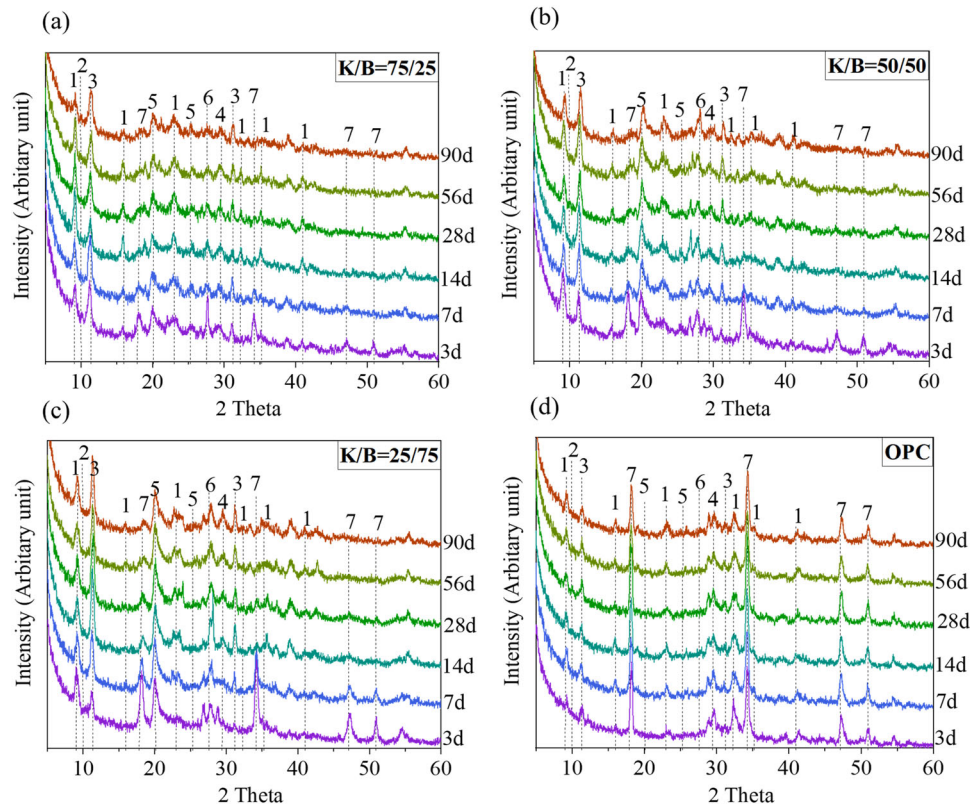


Figure 2. XRD patterns showing the crystalline phases present in calcined clay-portlandite binders mixed and cured with seawater (1: ettringite ($\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12}\cdot 26\text{H}_2\text{O}$)-PDF-96-901-1104; 2: Calcium aluminate monosulfate ($3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{CaSO}_4\cdot 12\text{H}_2\text{O}$)-[39]; 3: Hydrocalumite ($\text{Ca}_4\text{Al}_2(\text{OH})_{12}(\text{Cl})_2\cdot 4\text{H}_2\text{O}$)-PDF-96-900-9354; 4: Calcite (CaCO_3)-PDF-96-210-0993; 5: Grosite (CaAl_4O_7)-PDF-96-350-0015; 6: Phillipsite($(\text{Ca},\text{Na}_2,\text{K}_2)_3\text{Al}_6\text{Si}_{10}\text{O}_{32}\cdot 12\text{H}_2\text{O}$)-PDF-96-901-1150; 7: Portlandite ($\text{Ca}(\text{OH})_2$)-PDF-96-100-1769).

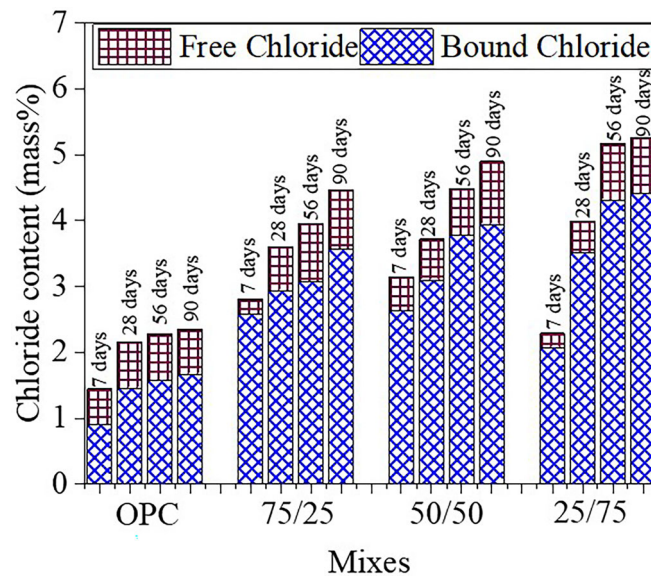


Figure 3. Total chloride content (bound Cl + free Cl) in the mixes determined by XRF.

hydrates (C_4AH_{13}) and enhances the chloride binding by forming Friedel's salt [24,54,55]. The concept of water-soluble chloride is still ambiguous [54,56]. According to Wilson et al. water-soluble chloride includes at least chloride in the porosity and chloride adsorbed onto C-A-S-H; it may also include a fraction of chemically bound chlorides [54]. Another study, however, shows that 20% of physically adsorbed chloride remains bound to the C-A-S-H

structure after the water-soluble test [56]. After considering the above, this study classified the total chloride content into two distinct parts: free chloride, which dissolves readily in water, and bound chloride, which does not dissolve easily in water. The extent of total chloride ion infiltration in RRC and OPC paste samples and their chloride binding capacity was observed up to 90 days, and the results are shown in Figure 3. The total chloride content

was considered a summation of bound and free chloride content. The results of our study indicate higher chloride infiltration in the RRC mixes than in the OPC mix. Specifically, at 90 days, the total chloride infiltration in all the clay mixes was 90–130% higher than that in OPC. This could be because material's permeability is the main cause of chloride ingress in cement-based materials, and the higher permeability of the clay mixes enhanced the ingress of seawater into the binder matrix. It did not cause an evident increase in the free chloride content, however, as the bound chloride content of the clay mixes was calculated to be 130–190% higher than that of the OPC (Figure 3). Comparing the total chloride infiltration and chloride binding capacity of the clay mixes yielded similar observations. The mix with a high bentonite content had higher total chloride and total bound chloride content, indicating the chloride binding capacity of the clay mixes depends on the extent of the chloride infiltration.

3.2.2.2. Quantification of chloride ion adsorption on C-A-S-H. SEM-EDS was performed on the polished paste sample that had been cured for 56 days to determine the Ca/Si ratio of the gel phases, and 150–200 EDS data points were collected. The BSE images and distribution of the EDS points of the calcined clay samples are shown in Figure 4. Geopolymer gel and calcium alumina silicate hydrate (C-A-S-H) can coexist as the amorphous gel hydration product of the calcined clay-portlandite system [30], so the EDS data points were grouped into three categories, depending on their Si/Ca ratio.

Previous studies proposed the presence of different phases of C-S-H and C-A-S-H gel with Ca/Si within the range of 0.66 to 2 (Si/Ca ratio of 0.5 to 1.51) [57]. Therefore, data points with a higher Si/Ca were addressed as geopolymer gel due to their high silica and low calcium content. Data points with a Si/Ca ratio lower than 0.5 were addressed as the crystalline phase, which includes the Friedel salt and AFm phases. Generally, Friedel's salt has an Al/Ca ratio of 0.5 [58]. As observed from Figure 4, however, the Cl/Al was higher in C-A-S-H than in the geopolymer gel, indicating chloride adsorption on C-A-S-H. The Ca/Si of most of the EDS points fell within the range of C-A-S-H for the 25/75 mixes, as shown in Figure 4(h), indicating that the amount of geopolymer gel was lower.

Figure 5 shows the weighted average of the Ca/Si, Al/Ca ratio, and Cl/Al ratio of the clay mix in the C-A-S-H gel. Despite having lower kaolin content, the 50/50 mix had a higher Al/Ca ratio than the 75/25 mix, confirming findings that increasing the quantity of bentonite can increase kaolin dissolution [59]. According to the XRF analysis described in Section 3.2.2.1, the mixes with higher kaolin content had lower total chloride infiltration and lower porosity, which resulted in the grains of clay in the 75/25 mix lacking the space to dissolve, react, and form hydration products. In addition, a low Ca/Si ratio promotes Al incorporation into C-(A)-S-H, while a high Ca/Si ratio influences Al to incorporate into AFm phases [57]. The Ca/Si ratio in the 50/50 mix was the lowest among all the three clay mixes, which increased the Al/Ca ratio. The 25/75 mix had the lowest kaolin content and Al/Ca ratio in C-A-S-H, but the Cl/Al ratio was

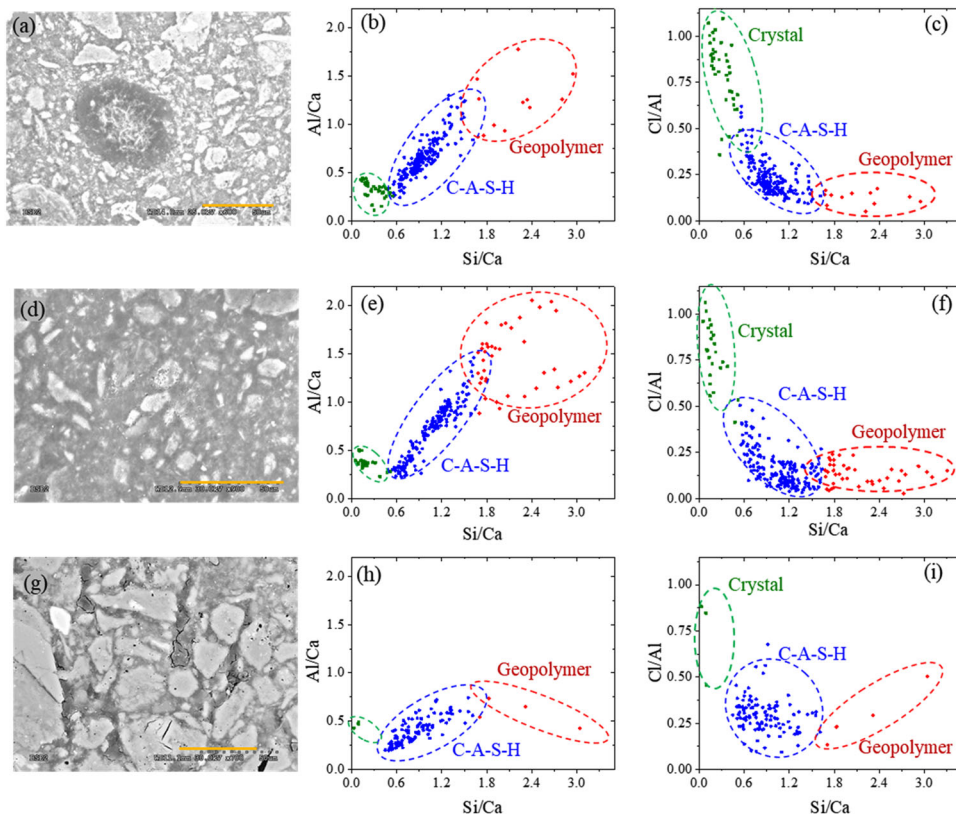


Figure 4. BSE image with the corresponding EDS analysis for the calcined clay samples: (a, b, c) 75/25 batch, (d, e, f) 50/50 batch, and (g, h, i) 25/75 batch. The scale bar represents 50 μm .

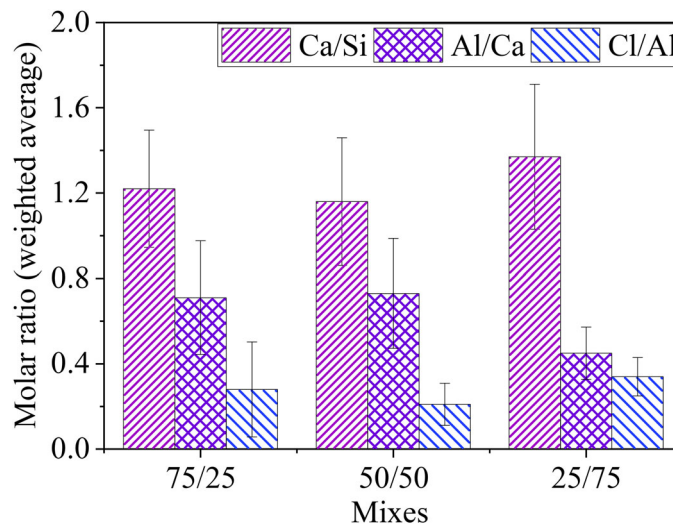


Figure 5. Molar ratio of the ions in the C-A-S-H gel phase of the clay mixes.

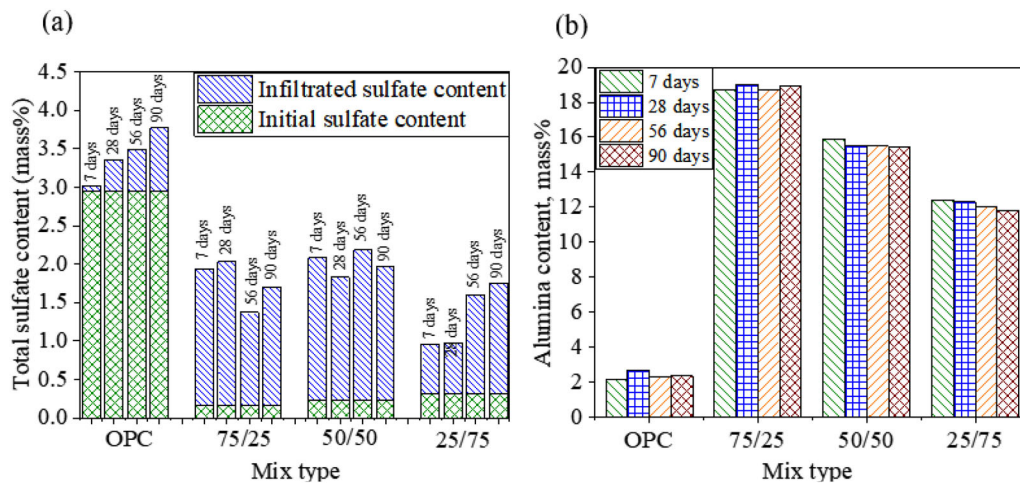


Figure 6. (a) Infiltrated sulfate content over time, and (b) total alumina content in the mixes.

significantly higher than that of the other two clay mixes. Previous studies showed that Cl⁻ ions tend to be closely adsorbed on the high Ca/Si ratio surface of C-S-H [60]. It can therefore be stated that the Cl⁻ ions were adsorbed to a greater extent on the C-A-S-H gel in the 75/25 and 25/75 mixes than in the 50/50 mix, due to their having a higher Ca/Si ratio in the gel phases.

3.2.3. Quantity of sulfates using X-ray fluorescence

Figure 6 presents the sulfate content in the calcined clay and OPC mixes. Since seawater was used as the mixing and curing agent, it was expected that the sulfate would ingress into the binder matrix. Also, the greater permeability of the calcined clay mix made it easier for the sulfate ions to access the binder matrix, resulting in the formation of ettringite. It should be noted that no peaks of gypsum were observed in the XRD measurement. Therefore, XRF sulfate measurement represents sulfate present as the ettringite or absorbed on the surface of the hydration products.

Figure 6(a) shows that the sulfate content before seawater exposure was higher in the OPC system than in the calcined clay mixes, due to the presence of gypsum;

however, the infiltrated sulfate contents were higher in the calcined clay samples than in the OPC samples. Figure 6(b) presents the total alumina content in the OPC and calcined clay mixes. As expected, the calcined clay samples showed higher alumina content compared to the OPC, which led to more sulfate binding by forming sulfoaluminate mineral phases (eg ettringite). This confirms that, similar to the ancient Roman concrete system, the sulfate sequestration capacity of the calcined clay-based binder, RRC, is greater than that of the traditional OPC system.

3.2.4. Morphology of chloride- and sulfate-binding phases in RRC mix

SEM-EDS of the samples were carried out at 90 days to observe the morphology of the chloride- and sulfate-binding hydrates, as shown in Figure 7. The use of seawater for mixing and curing resulted in the formation of ettringite and Friedel's salt, which was confirmed by the EDS spectra. The microstructure seemed very dense, as all the pores were filled with these crystalline products. The ettringite needles were more prominent than the plate-like Friedel's salts, though the availability of Friedel's salt was more abundant in the pore structures.

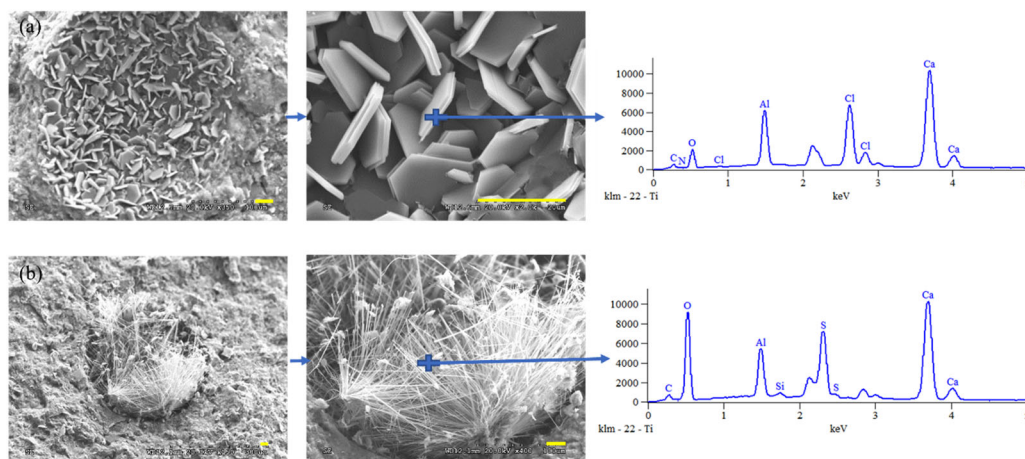


Figure 7. Morphology of (a) Friedel's salt and (b) ettringites at 90 days observed in the RRC mix. The scale bar represents 20 μm .

Table 8. Chemical extraction of the geopolymer gel.

Mixes	The residue after salicylic acid extraction	The residue after HCl extraction (unreacted clay)	Geopolymer gel
75/25	59%	47.18%	11.82%
50/50	55%	39.3%	15.7%
25/75	56.1%	46.47%	9.63%

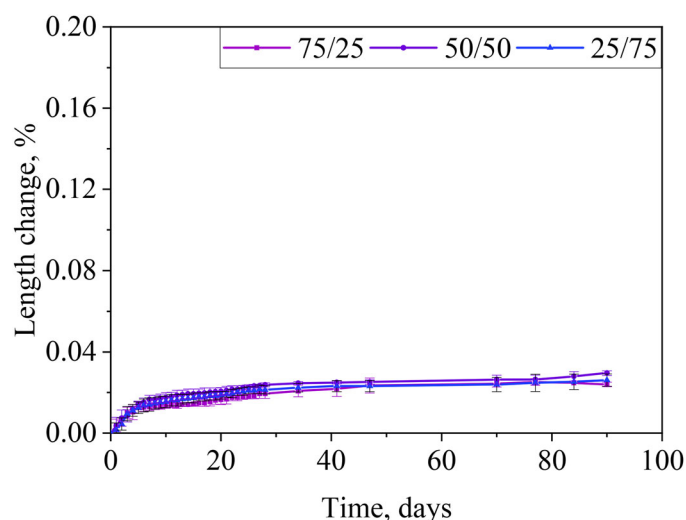


Figure 8. Percentage length expansion of mortar bars due to exposure to seawater.

3.2.5. Degree of reaction

A chemical extraction method was used to calculate the percentage of insoluble residue in the initial mass of unreacted clay, and Table 8 presents the weight percentage of the sample that remained after it was dissolved in the salicylic acid and hydrochloric acid (HCl). Salicylic acid does not dissolve geopolymers or unreacted clay, but hydrochloric acid dissolves everything except the unreacted clay [30,31,61]. The weight percentage of unreacted clay indicates the degree of reactivity of the calcined clay, and it was observed that the unreacted clay content was lowest in the mix that contained 50% bentonite content. This finding

agrees with a previous study [59] that showed that the dissolution of metakaolin increases in the presence of a certain quantity of bentonite. The relative amount of the geopolymer gel was calculated by subtracting the residue after the salicylic acid and HCl extraction. The 50/50 mix showed the highest geopolymer gel formation. The 25/75 mix showed the lowest geopolymer gel formation which matched the observation from SEM-EDS analysis.

3.2.6. Length change due to seawater curing

As seen in Figure 8, nearly all of the calcined clay mixes recorded rapid expansion in length for the first 10 days

and expanded gradually for subsequent testing ages. The early-age expansion was attributed to seawater absorption by the mortar samples; the maximum expansion was significantly lower than the usual limit of 0.2%. As discussed in previous sections, using seawater leads to the formation of ettringite and Friedel's salt. It has been well documented that Friedel's salt does not lead to any significant length change [62]; however, salt crystallization in the binder matrix can cause pore pressure that leads to length expansion. At the end of 90 days of seawater curing, none of the investigated samples showed self-destructive failure caused by length expansion, which may be attributed to the large amount of salt crystallization filling the pores rather than creating pore pressure.

3.3. Environmental impacts of the developed cementitious materials

3.3.1. Environmental impacts of the binders

The global warming potential (GWP) of binder mixes producing 1 m³ of mortar with 1 MPa compressive strength is presented in Figure 9, where it can be observed that the OPC binder has a GWP of 10 kg CO₂-eq and the GWP of the calcined clay-portlandite binder is 85 to 90% lower. It is important to note that the calcined clay batches with a

higher kaolin content showed higher compressive strength after 28 days of curing; therefore, it can be concluded that increasing the kaolin content enables the use of less binder to achieve 1 MPa compressive strength, which lowers the GWP.

The differences in functional units make it challenging to compare the estimated GWP values with the literature. But one source, Bianco et al. [63], reported that the GWP of OPC concrete mixes (1 m³ functional unit) varies from 333 to 507 kg CO₂-eq for 35 to 70 MPa strength classes, respectively [63]. Therefore, for 1 MPa, the previously reported value would range from 9.5 to 7.2 kg CO₂-eq, which matches well with the OPC GWP determined in this work.

The impact values for each of the other environmental categories caused by RRC binders were normalized with respect to the OPC binder and are shown in Figure 10. Environmental impacts increased with a decreasing K/B ratio since a higher binder content was needed to achieve 1 MPa of compressive strength. The environmental impact of calcined clay binders is less than that of the OPC binder, except for the carcinogenic and eutrophication impacts caused by the 25/75 calcined clay-portlandite mix. It should be noted that the carcinogenic impacts for 1 kg of clay-portlandite binder and 1 kg of OPC binder are

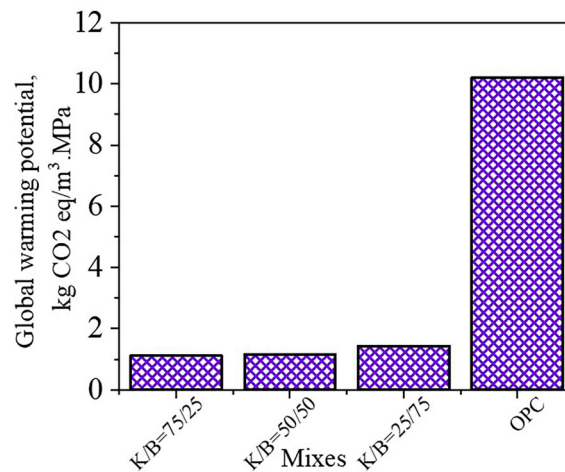


Figure 9. Global warming potential (GWP, Kg CO₂ eq/ (m³.MPa) for different binder mixes.

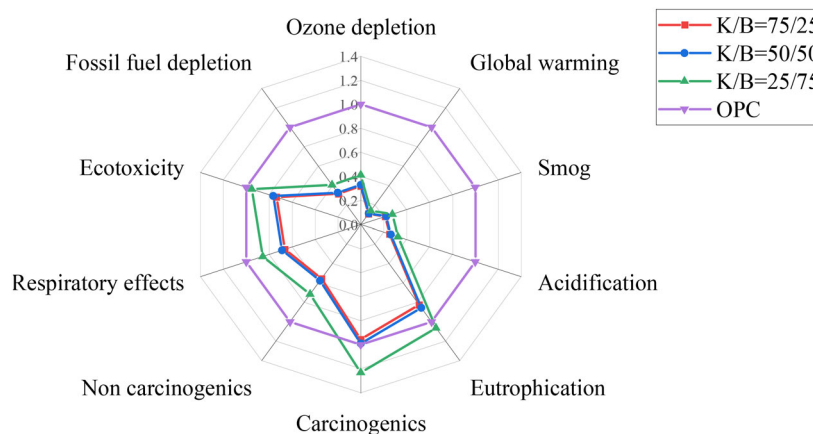


Figure 10. Normalized impact values for pure binder.

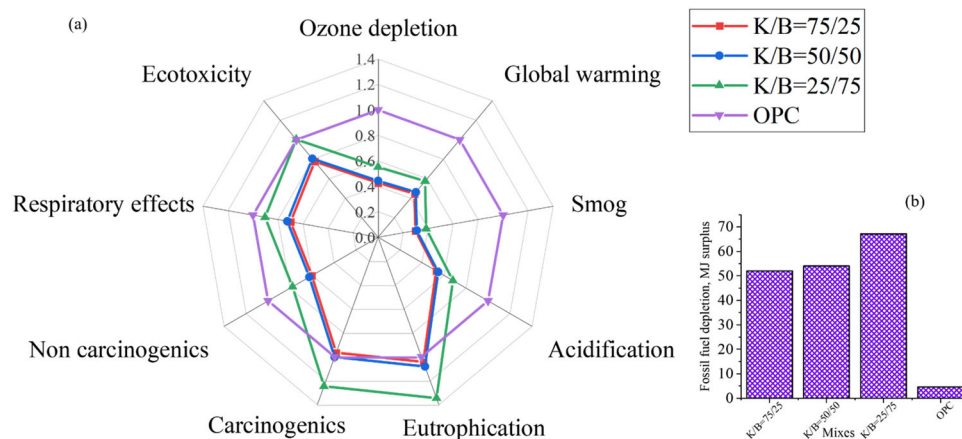


Figure 11. (a) Normalized impact values for mortar samples caused by all the impact categories except fossil fuel depletion, and (b) normalized impact caused by fossil fuel depletion.

3.76×10^{-06} and 6.81×10^{-06} , respectively, which translates into the carcinogenic impact per kg of calcined clay binder being smaller than that of the OPC binder; however, the large quantity of binder needed to achieve 1 MPa strength in the 25/75 mix makes the overall carcinogenic impact of the 25/75 mix higher. Similarly, the overall eutrophication impact of the 25/75 mix makes the environmental impact greater. Nevertheless, the 75/25 and 50/50 mixes recorded lower environmental impacts in every category than the OPC mix.

3.3.2. Environmental impact caused by mortar

The environmental impacts caused by mortars are presented in Figure 11(a). As stated earlier, the inclusion of superplasticizers and aggregates in calcined clay mortar render the GWP higher than in binder mixes; even so, the GWP of calcined clay mortars is 42 to 55% lower than that of the OPC when the same type of aggregates is considered. The use of superplasticizers also affects other impact categories like carcinogenic and eutrophication. The fossil fuel depletion caused by the superplasticizer is significantly higher than the other impact categories (114–147% greater than the OPC mortar); therefore, it was plotted separately as a bar chart in Figure 11(b).

4. Conclusions

The ability of calcined clay-portlandite binders, also referred to as ‘recreated Roman cement/concrete or RRC,’ to reduce the carbon footprint and increase the durability of concrete exposed to seawater was evaluated and compared with traditional OPC mixes in this study. The concluding remarks are listed below.

1. The calcined clay-based samples achieved 25 to 30 MPa compressive strength, with 90% of the maximum strength achieved within 28 days of curing. This indicates that they are a viable alternative to normal-strength concrete.
2. The lifecycle assessment showed that using RRC as a binder reduced the GWP by nearly 90% compared to the OPC binder. Even when the effect of

the superplasticizers and fine aggregates were considered, they could reduce the GWP up to 40 to 50%. Such a significant decrease in GWP indicates that the calcined clay-portlandite binder can significantly reduce the carbon footprint of marine concrete.

3. The XRD and XRF measurements showed that the mixes prepared with calcined clays exhibited higher chloride binding capacity than the OPC because of the higher formation of Friedel’s salt, which leads to microstructure densification.
4. Larger amounts of reactive alumina in calcined clay led to an increased amount of bound chloride. The total chloride content in all the clay mixes was 90–130% higher than that in the OPC. The chloride binding capacity of the clay mixes was 130–190% higher compared to the OPC mix.
5. The SEM-EDS elemental distribution analysis confirmed the co-existence of C-A-S-H gel and geopolymer gel in RRC reaction products. In addition, Cl/Al was observed to be higher in C-A-S-H than in geopolymer gel, indicating chloride adsorption on C-A-S-H. The clay mix with high Ca/Si resulted in high Cl adsorption.
6. The calcined clay mixes with a minimum of 50% kaolinite content showed adequate strength, durability, and low environmental impacts. However, for a lower kaolinite content (e.g., 25%), the environmental impact was relatively high due to the low strength of this mix.

Disclosure statement

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