Case Studies in Construction Materials 19 (2023) e02393

Contents lists available at ScienceDirect

Case Studies in Construction Materials

journal homepage: www.elsevier.com/locate/cscm

Improvement of the durability of concrete by substitution of raw ground colemanite

Cuma Kara [a], Sezai Kutuk [b,*], Tuba Kutuk-Sert [c]

[a] Department of Construction, Artvin Coruh University, 08400 Borcka, Artvin, Turkey
[b] Department of Marine Engineering, Faculty of Turgut Kiran Maritime, Recep Tayyip Erdogan University, 53900 Derepazari, Rize, Turkey
[c] Department of Civil Engineering, Faculty of Engineering and Architecture, Recep Tayyip Erdogan University, 53100 Rize, Turkey

ARTICLE INFO

Keywords:
Raw ground colemanite
Particle size
Concrete
Strength
Durability

ABSTRACT

This study investigated the effects of raw ground colemanite (GC) mineral on concrete strength and durability. Concrete mixtures were prepared at six replacement levels of GC (0%, 1%, 2%, 3%, 4% and 5%, by weight of cement). Fresh state properties of concrete samples were measured. Schmidt Hammer, ultrasound pulse velocity, abrasion, flexural, and compressive strength tests were performed on the cube, cylinder and prismatic concrete samples on the 7th, 28th, and 90th days. As concrete durability has a negative impact on many physical and chemical factors, the durability properties of the samples after wet-dry, freeze-thaw, sulphate, and chloride exposure were investigated, resulting in the finding that GC substitution up to 5% yields the desired compressive strength for the C30/37 concrete class. The optimal GC substitution ratio was determined to be 3%, as this ratio increases the strength and durability probabilities. It was decided that raw GC mineral substitution with an average particle size of 12 μm and increasing adhesion force in concrete production is convenient, particularly in the context of improving material properties against environmental circumstances, saving cement, and utilizing boron minerals.

1. Introduction

Cement is the most utilized construction material. Cement production requires high amounts of energy. For this reason, cement is the product with the highest cost among the materials in concrete [1]. Additionally, its production has harmful effects on the environment and human health due to the emission of CO_2 [2,3]. Substitution of mineral powders for cement is currently being widely investigated in order to reduce the harmful effects of cement production. The amount of cement required in concrete production is reduced with mineral powders substituted for cement. In addition, the strength and durability of cement-based materials can be improved through the use of substitute materials [4]. Thus, in recent years, the use of boron minerals in cement-based materials has attracted the attention of researchers [5,6].

The boron element is mostly found in nature as boron trioxide (B_2O_3) in boron minerals. Turkey approximately contains 73% of global B_2O_3 reserves. The most abundant boron minerals in terms of reserves in Turkey are tincal, ulexite and colemanite [7]. Concentrator plants are utilized for the enrichment of the ore. The concentrated product is subjected to the crushing and grinding processes in order to obtain the ground product and to package it in the packaging unit respectively. In the end, this colemanite mineral

* Corresponding author.
E-mail addresses: sezai_kutuk@hotmail.com, sezai.kutuk@erdogan.edu.tr (S. Kutuk).

https://doi.org/10.1016/j.cscm.2023.e02393
Received 10 May 2023; Received in revised form 25 July 2023; Accepted 11 August 2023
Available online 12 August 2023

becomes a commercial product to be sold with the label “ground colemanite (GC)” (two types, −75 μm and −45 μm) [8]. Through grinding, it is possible to reduce the particle size or crystallite size of a material [9,10]. Thus, it is clear that the physical, mechanical, electrical and magnetic properties of the material are improved [11]. The particle size and specific surface area of the material added to the mixture in the production of cement-based materials are crucial physical parameters affecting both strength and durability. As can be seen in studies conducted to improve the properties of cement-based materials or to utilize waste materials, the particle sizes of materials that may be alternatives to existing substituted materials (such as silica fume, fly ash, blast furnace slag) are reduced by grinding processes [12,13]. In contrast, the commercial GC mineral can be used as supplied without further grinding.

Studies about the inclusion of colemanite in mixtures instead of cement or aggregate in cement-based materials are ongoing [14,15]. Studies on radiation transmission of cement-based materials containing colemanite have received extensive interest. Cement-based materials produced with colemanite are reportedly good radiation shields [16,17]. Furthermore, it was stated that with the inclusion of colemanite in cement production, the amount of CO_2 released into the atmosphere was lowered by 25–30% [18]. In previous studies involving the addition of different proportions of colemanite substitute, the most appropriate substitute ratios have been suggested by researchers. It is recommended to utilize 30% colemanite as an aggregate substitute and up to 5% colemanite as a clinker or cement substitute [19,20]. Since colemanite significantly increases the setting time of cement-based materials, it is the most prominent factor in the suggestion of these ratios. Using a high amount of colemanite prolongs the setting time of cement-based materials significantly. For this reason, it was reported that high amounts of colemanite use may negatively impact strength development due to the delay in setting time [21]. Furthermore, especially in studies on radiation transmission, it can be seen that the fresh state characteristics of the material are not included [22–24]. Investigations were mostly performed on mortar materials. In the literature, studies on concrete materials containing colemanite can be found. However, when these studies are examined, there are few studies on concrete strength and durability [25–27]. In order to better understand the effects of colemanite on concrete, it is obvious that studies with different concrete mixtures (such as cement dosage, water/cement ratio, aggregate type) are needed. Recently, many studies on concrete have focused on determining the reaction of concrete against durability problems [28,29]. It is important to experimentally determine the adverse conditions affecting the durability of the concrete. Wet-dry, freeze-thaw, sulphate and chloride pose risks to the durability of the concrete [30,31]. As of yet, a few studies have been conducted to determine the strength losses that will occur in concrete when concrete produced with colemanite was exposed to these durability problems.

In the literature, studies on cement/mortar/concrete being substituted or the addition of colemanite mineral/waste (with different chemical and physical properties) can be found. However, there are very few studies on the substitution of raw GC mineral, a standard mineral and is commercially available in tons, to cement and the durability of GC mineral substituted concrete. As a substitution material, impurity components, the thermal properties, particle shape, and particle size of the GC mineral were investigated. The GC mineral was substituted for cement at ratios of, 1%, 2%, 3%, 4% and 5% by weight. The durability of concrete samples produced with GC mineral was tested with wet-dry, freeze-thaw, sulphate and chloride conditions, which was followed by a discussion of the results.

2. Experimental procedure

2.1. Materials

In the study, the materials used in concrete production consisted of Portland cement, raw ground colemanite (GC) mineral, aggregate, superplasticizer (Grace Zyla 420), and tap water.

2.1.1. Cement

Portland cement (CEM I 42.5 R) has a density of 3.12 g/cm^3 and a surface area of 3269 cm^2/g. Chemical properties of cement are given in Table 1.

2.1.2. Raw ground colemanite mineral additive

The use of minerals with abundant reserves in concrete technology is crucial for sustainability. The B_2O_3 component, which is found in the structure of the colemanite mineral, is reported to affect the fresh and hardened properties of cement-based materials. In the literature, it was determined that the B_2O_3 percentages in the preferred structure of colemanite are quite different [26,32,33].

For this study, the colemanite mineral was obtained in raw form GC (−75 μm) from the Eti Mine Bigadiç Boron Operations Directorate. Its density is 2.39 g/cm^3 and its surface area (Blaine) is 3432 cm^2/g. The oxidized components of the GC mineral provided by the manufacturer are given in Table 2. Furthermore, in another study, according to data obtained from the energy dispersive spectrometer (EDS) and the X-ray diffractometer (XRD) [34], it can be clearly seen that the GC mineral is not pure colemanite ($2CaO{\cdot}3B_2O_3{\cdot}5H_2O$), and also that it has small amounts of the Si, Mg, Sr, S, Al, Na, and Fe elements. When the data in Table 2 are considered, it can be understood that the GC mineral may contain natural impurities ranging from about 4–13% by weight.

The thermal properties of the GC mineral were examined with Thermogravimetry (TG) and the Differential Thermal Analysis (DTA) simultaneous thermal analyzer (Netszch, model "STA 449 F3 jupiter"). TG/DTA measurements were performed at 25–1000 °C

Table 1
Chemical properties of cement.

Oxide	CaO	Al_2O_3	Fe_2O_3	SiO_2	SO_3	MgO	Na_2O	Loss of ignition	Insoluble matter
Value (%)	62.64	4.56	3.36	19.05	2.88	2.98	0.15	3.02	0.30

Table 2
Chemical properties of ground colemanite mineral.

Oxide	B_2O_3	CaO	Al_2O_3	Fe_2O_3	SiO_2	SO_4	MgO	Na_2O	SrO	Loss of ignition
Value (%)	40 ± 0.5	27 ± 1	≤ 0.4	≤ 0.08	4–6.5	≤ 0.6	≤ 3.0	≤ 0.5	≤ 1.5	≤ 25.0

temperature, 10 ºC/min heating rate and nitrogen atmosphere conditions. Fig. 1 depicts the TG/DTA curves of the GC mineral. TG (mass change) value reduced to 99% at 300 °C, to 98% at 375 °C, to 86% at 425 °C, to 81% at 500 °C, to 79% at 650 °C, to 74% at 825 °C and to 73% at 1000 °C. A small peak at 405 °C, a narrow peak with high intensity at 410 °C and a small peak at 810 °C appeared in the DTG (difference in mass change) curve. A high endothermic peak at 396 °C, an endothermic peak at 725 °C, an exothermic peak at 754 °C, and an endothermic peak at 812 °C were found in the DTA curve. From this data, it was determined that a large decomposition occurred around 400 °C. This result was caused by the breaking-off of OH bonds from the crystal structure of pure colemanite mineral, in other words, a certain molar value of 5 mol H_2O crystal water being removed from the structure (dehydration mechanism) [35,36].

The mass loss of 1% at 300 °C observed in the TG curve was attributed to moisture or superficial water [37]. From this result, it was determined that there was no decomposition from the crystal structure of the GC mineral at wet-dry, freeze-thaw and oven temperatures. The loss value of 27% at 1000 °C obtained in the TG curve verifies the ignition loss value of 25% by weight in Table 2.

Morphological analysis of the GC mineral was carried out through a stereo optical microscope (SOM) (Olympus, model 'SZ61') with a digital camera and a scanning electron microscope (SEM) (Jeol, model 'JSM-6610'). SOM image, which is more practical and cheaper, was recorded under white light, and the SEM micrograph was recorded at 20 kV after the application of gold coating. First, SOM images of the GC mineral are presented in Fig. 2(a) and (b). In the SOM image at x15 magnification (visible to the naked eye), it was observed that the mineral was grey in colour and its particle size was less than 100 μm. However, in the SOM image under x45 magnification, it was discerned that the mineral also includes a small number of different colours. These different colours are thought to be due to the presence of impurities given in Table 2. In addition, each colour means either a different mineral or other component in its mineral composition. It is known that colemanite mineral deposits also include compounds such as calcite, clay minerals, cristobalite, and celestite [38].

The analyzed SEM micrograph and particle size distribution (PSD) of the GC mineral are illustrated in Fig. 3(a) and (b), respectively. In the SEM micrograph of the GC mineral under x500 magnification, it was observed that the particles did not have a homogeneous distribution. It was realized that the particles generally have sharp edges and irregular shapes, but ones with a size of less than 25 μm are relatively close to rounded shape. To learn more about particle size, a detailed analysis was conducted using a piece of software on the SEM micrograph (Fig. 3(a)). It was detected that the particle size ranged from 77.851 μm to 335 nm. This finding indicates that the GC mineral has a sub-micron size, and moreover, this finding agrees with the d_{min} = 420 nm (the smallest particle size) value derived from the PSD measurement conducted through a laser size analyzer in another study [27]. PSD was used to inspect over 100 individual pieces of data and the particle size was determined to be generally less than 40 μm (Fig. 3(b)). Furthermore, the Gaussian fit curve with 3 parameters for PSD was drawn and found to be R^2= 0.99. It is obvious that the strength of cement-based

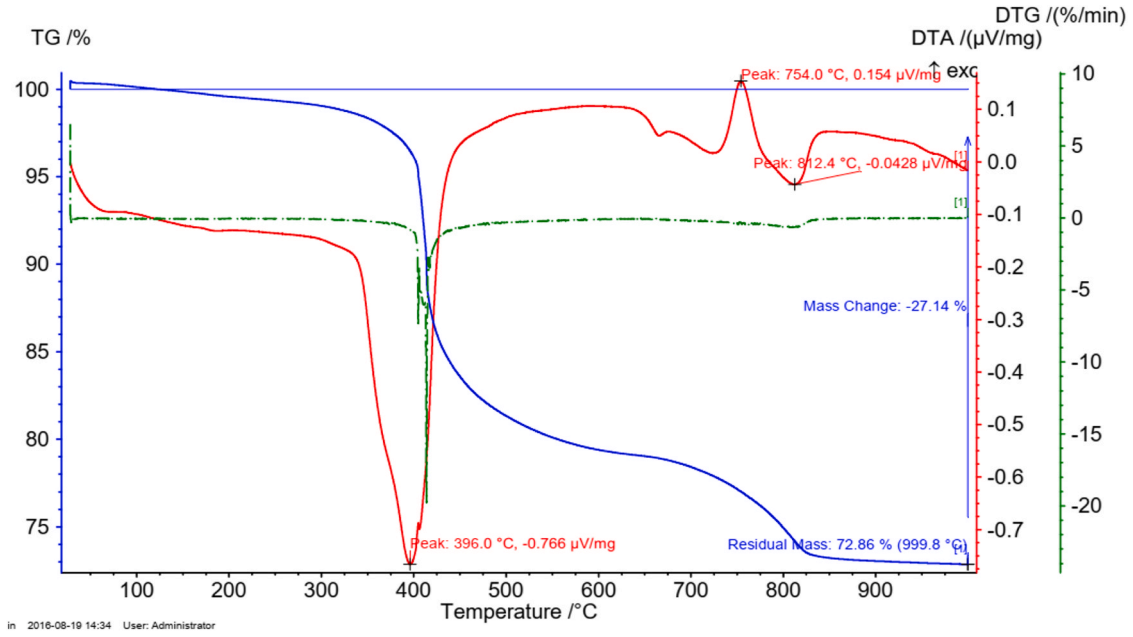

Fig. 1. TG/DTA curves of GC mineral.

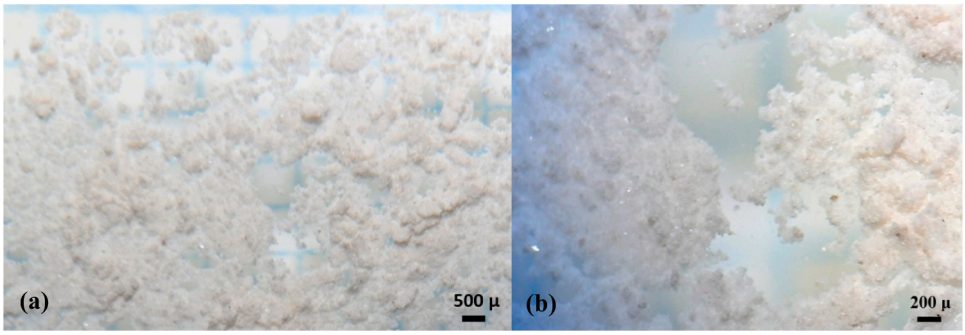

Fig. 2. SOM images of GC mineral under (a) x15 magnification and (b) x45 magnification.

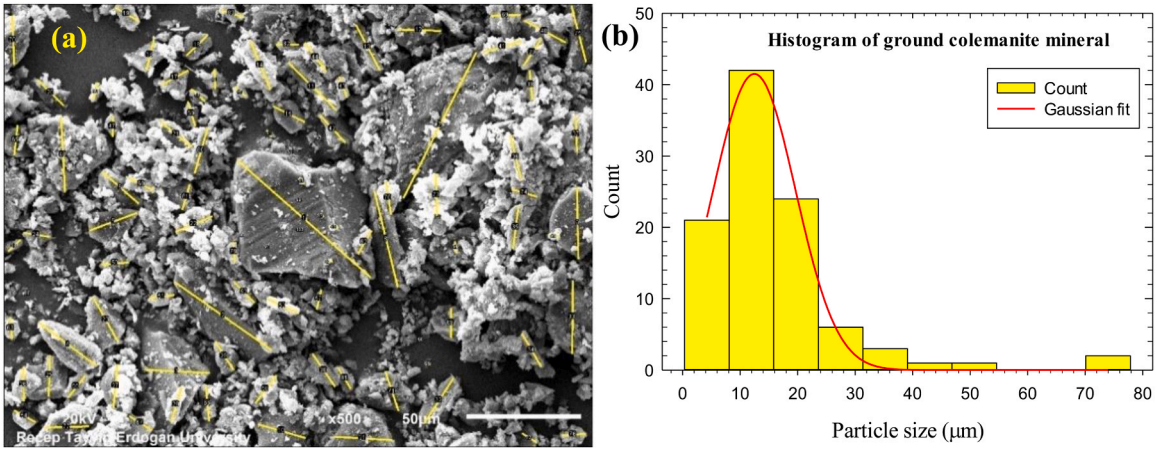

Fig. 3. (a) Analyzed SEM micrograph and (b) particle size distribution of the GC mineral.

materials is strongly affected in a positive manner by particle sizes in the range of 3–30 µm [39]. In the study, the average particle size value was calculated to be 12.386 µm. This value is very close to the $d_{50} = 20.683$ µm (the cumulative volume per cent passing as 50%) value obtained from the PSD measurement by a laser size analyzer in another study [27]. The fact that the average particle size calculated from SEM analysis is slightly smaller than the value obtained by the laser PSD measurement can be attributed to the agglomeration of the particles [40].

2.1.3. Aggregates

Concrete production was conducted with fine (0–5 mm), coarse-1 (5–12 mm), and coarse-2 (12–25 mm) andesite aggregates. The experimental granulometry curve of the aggregates used in the study can be seen in Fig. 4, and its physical properties are listed in Table 3.

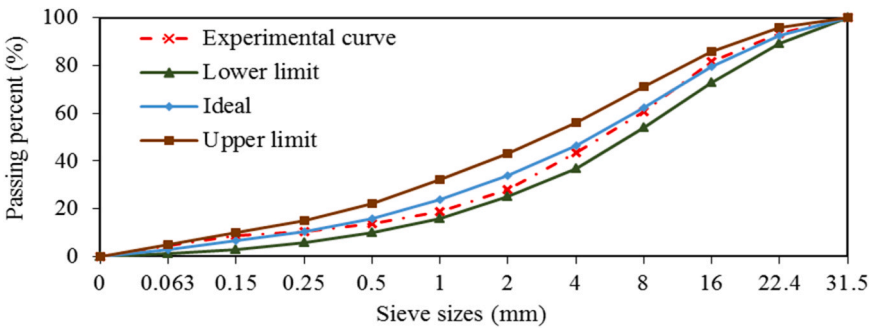

Fig. 4. Granulometry curve of aggregates.

Table 3
Physical properties of aggregates.

Type of aggregate	Density *(g/cm³)*	Water absorption *(%)*
Fine aggregate	2.63	2.30
Coarse aggregate-1	2.70	1.65
Coarse aggregate-2	2.72	1.20

2.2. Mix proportions

The GC-free concrete mixture contained 350 kg/m^3 cement as a binder. In other mixtures, cement was reduced by 1%, 2%, 3%, 4%, and 5% of the cement weight and replaced with GC minerals of the same amount. The superplasticizer was used as up to 0.8% of the binder amount in the mixtures. For convenience, GC-0 was used for the concrete sample that does not include GC minerals. The GC-1, GC-2 GC-3, GC-4 and GC-5 notations were assigned to the concrete samples containing 1%, 2%, 3%, 4% and 5% GC, respectively. Substitution ratios of GC mineral to cement and the symbols of the samples are depicted in Table 4.

2.3. Methodology

In this study, fresh concrete mixtures were prepared by replacing the GC mineral with cement in various proportions. After the density [41], slump [42] and air amounts [43] of fresh concrete were determined, they were placed in molds. Molds with a size of 150×150×150 mm for compressive strength, 100×100×400 mm for flexural strength, ø100 × 200 mm for tensile strength in split and 71×71×71 mm for abrasion resistance were used. The continuation of the study consists of two parts: strength and durability.

2.3.1. Hardened properties of concrete mixtures

In the first section where the hardened properties were examined, the flexural [44], splitting tensile [45] strengths and abrasion [46] resistance of concrete samples were also determined. For the strength tests carried out on concrete samples, 3 samples were tested and averaged for all ages. Furthermore, measurements were made with the Schmidt hammer (SH) and ultrasound pulse velocity (UPV) tests, ones among non-destructive tests. Strength tests were performed on the 7th, 28th, and 90th days.

The second part of the study consisted of the examination of durability properties. The concrete durability was tested through exposure to the wet-dry cycle, the freeze-thaw cycle, sulphate and chloride. All durability tests were performed on 150×150×150 mm sized concrete samples. The mass, SH, UPV and compressive strength of the samples left in physical and chemical environments were ascertained. Concrete samples exposed to physical and chemical environments were compared with samples (control mix) that were water-cured. For the strength and durability experiments, a total of 288 concrete samples in different shapes and sizes were produced within the scope of this study.

2.3.1.1. Wet-dry cycles test. Concrete samples were dried at 100 ± 5 °C for 24 h, their masses were found at room temperature. The samples were kept in tap water for 48 h. Afterwards, they were dried in an oven at 100 ± 5 °C for 24 h. This process was accepted as the one wet-dry cycle, and a total of 20 wet-dry cycles were utilized (Fig. 5). The masses of the samples were measured at the end of each cycle [47,48].

2.3.1.2. Freeze-thaw cycle test. Concrete was subjected to freeze-thaw cycles. Before the test, concrete samples were dried at 100 ± 5 °C for 24 h and their masses were determined at room temperature. The samples were placed in metal sample containers filled with water at 20 ± 5 °C. In the test device, the temperature was gradually decreased from 20 °C to − 17.5 °C. This circumstance is expressed as “freeze” in Fig. 6. In the second step, the samples were exposed to a temperature increase from − 17.5–20 °C and a thaw environment was created. One cycle of the entire test lasted 24 h. The freeze-thaw cycle given in Fig. 6 was repeated 10 times with the adjusted air conditioner (Binder, model "MKF 240"). After the freeze-thaw cycle, the masses of the concrete samples were measured [49].

2.3.1.3. Effect of sulphate and chloride. $MgSO_4$ (sulphate) and NaCl (chloride) were used to find the resistance of concrete samples produced with GC mineral substitution to chemical environments. Sulphate and chloride had purity above 99%. The concrete samples,

Table 4
Mix proportions of concrete (kg/m^3).

Symbols	GC-0	GC-1	GC-2	GC-3	GC-4	GC-5
GC replacement rate	0%	1%	2%	3%	4%	5%
Cement	350.0	346.5	343.0	339.5	336.0	332.5
GC	0.0	3.5	7.0	10.5	14.0	17.5
Water	157.5	157.5	157.5	157.5	157.5	157.5
Fine aggregate	925.5	925.1	924.6	924.2	923.8	923.3
Coarse aggregate-1	408.7	408.5	408.3	408.1	407.9	407.7
Coarse aggregate-2	589.0	588.7	588.4	588.2	587.9	587.6

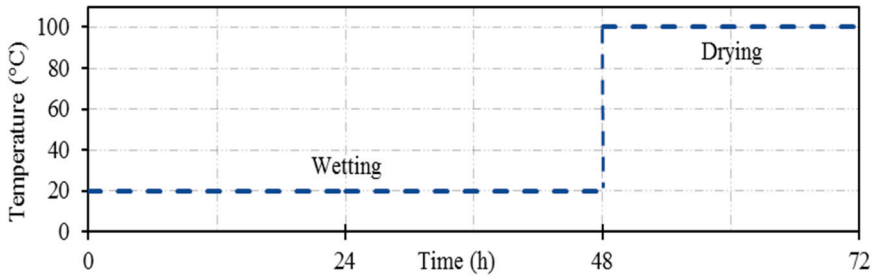

Fig. 5. Wet-dry cycle (1 cycle).

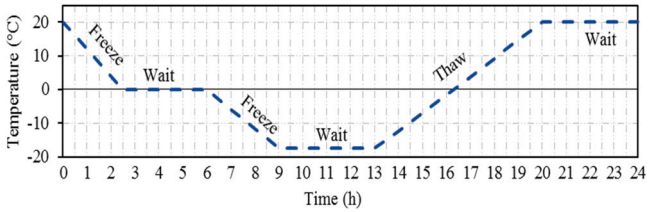

Fig. 6. Freeze-thaw cycle (1 cycle).

which were cured in water for 28 days, were dried for 24 h at 100 ± 5 °C, their masses were ascertained at room temperature, and they were then kept in chemical environments until the 90th day. The concentration of the chemical environment was prepared to be 5% $MgSO_4$ and 5% NaCl. Chemical solutions were re-prepared every 10 days. After the chemical exposures, the masses of the concrete samples were measured at room temperature as soon as they were dried.

3. Results and discussion

3.1. Fresh concrete properties

Fresh state properties of concrete samples are presented in Table 5. It was determined that the GC mineral substitute, when used up to 5%, decreased the workability and air content of the concrete. This can be elucidated by the fact that the density of GC mineral is smaller than cement. The low-density mineral contained more in concrete by volume than cement. In studies conducted with GC substitutes, the number of studies examining the colemanite effect on fresh state properties of concrete was found to be limited. In a study investigating slump values, it was observed that the use of colemanite as a cement substitute reduced the workability of concrete and that this was expressed through the high ignition loss value of colemanite [50]. In another study, it was observed that colemanite increases the workability of concrete, whereas no change in the slump class was found [26]. When the properties of colemanite used in these studies are analysed, it was found that there are differences in their physical and chemical values. Furthermore, when the measurements with colemanite substitution up to 5% are considered, the obtained slump values indicate that colemanite has no significant effect on workability. In conclusion, both this study and others in the literature demonstrate that substituting low amounts (5%) of colemanite by weight to cement will not significantly alter its workability. This circumstance can be explained through the fact that the specific surface value of colemanite (3432 cm^2/g) is close to cement (3269 cm^2/g).

3.2. Effect of raw ground colemanite mineral on the strength of concrete

The determined compressive strength and strength increase rate of the concrete samples were presented in Fig. 7. Compressive strength of GC substituted samples measured on the 7th day were found to be lower than non-GC substituted samples. With the retarding effect of colemanite, the low compressive strength of the samples containing GC was an expected result [25,33]. According to

Table 5
Fresh state properties of concrete samples.

Experiments	Types of concrete					
	GC-0	GC-1	GC-2	GC-3	GC-4	GC-5
Density (g/cm^3)	2.38	2.37	2.38	2.35	2.36	2.36
Air content (%)	1.5	1.4	1.3	1.3	1.2	1.3
Slump value (mm)	135	130	130	125	120	110
Slump class (S1~S5)	S3					

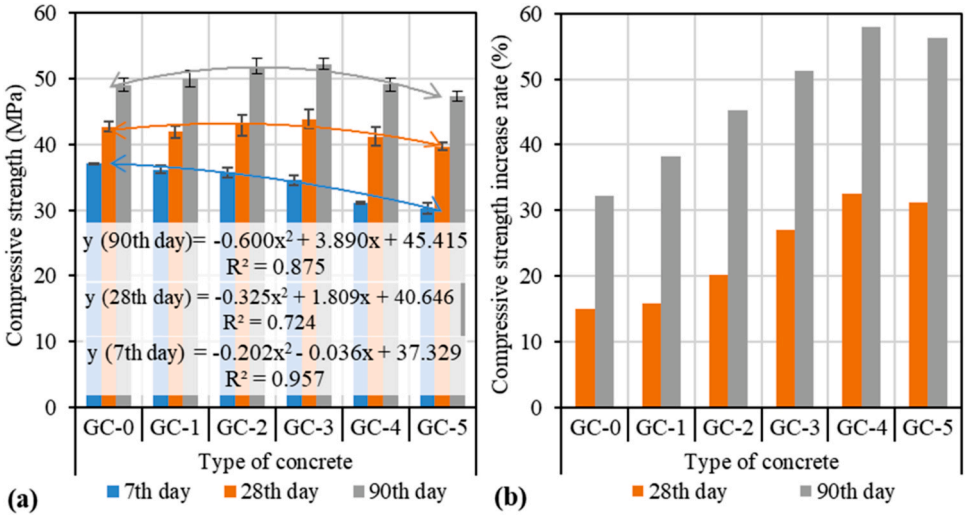

Fig. 7. (a) Compressive strength (b) The strength increase rate of the samples.

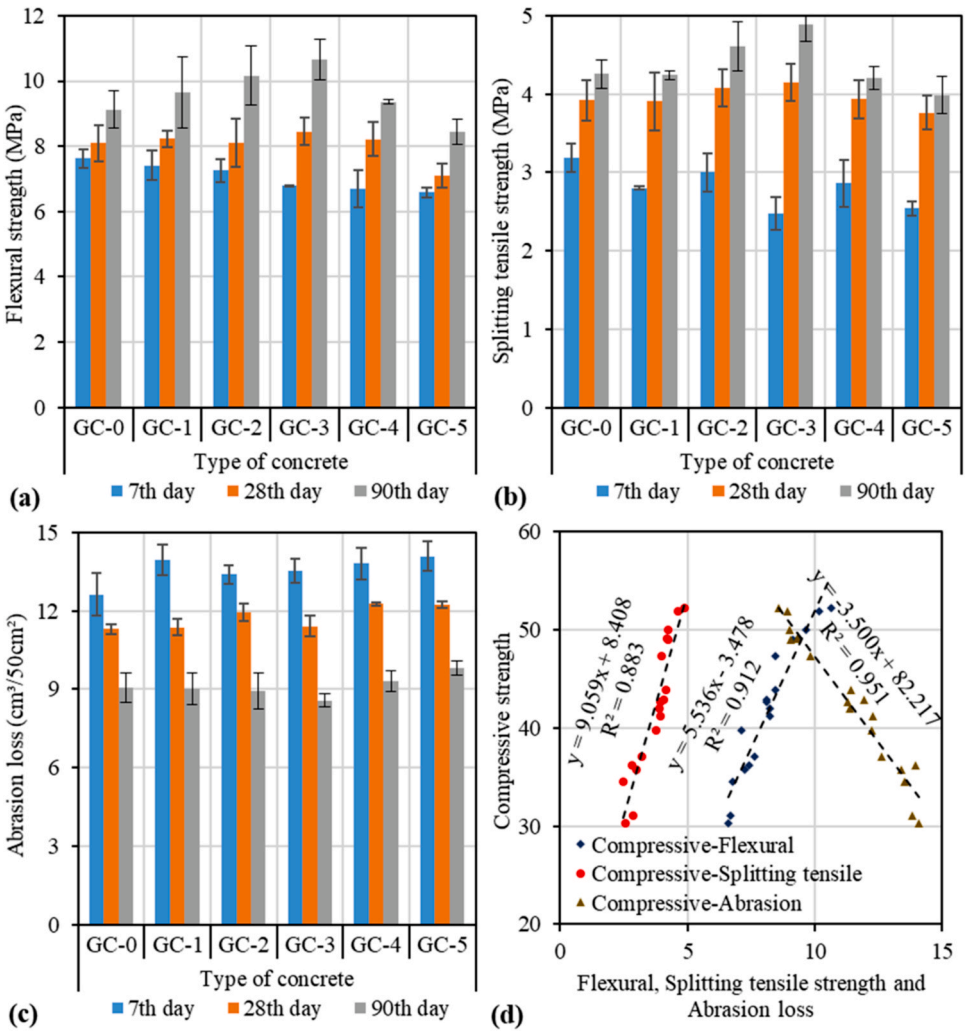

Fig. 8. (a) Flexural strength (b) Splitting tensile strength (c) Abrasion loss (d) Values of correlation between tests.

the literature and the results of this study, it is obvious that colemanite decreases the strength development of concrete at an early stage. When the 28-day compressive strength results of concrete samples are analysed, it can be observed that all samples met the target compressive strength (C30/37). The compressive strength of concrete, an important mechanical property, is usually determined after 28 days of standard curing [51]. The compressive strength results show that all GC ratios (1%~5%) can serve as substitute materials for cement. However, although GC substitutes met the target strength, not all GC-containing samples could reach a compressive strength above the sample without GC. From the 28-day compressive strength results, the highest compressive strength belonged to the GC-3 sample and the lowest compressive strength belonged to the GC-5 sample. When the 90-day compressive strength is examined, it can be seen that the highest one was GC-3 sample and the lowest one was the GC-5 sample, much like the 28-day results. The noticeable difference between days 28 and 90 pertains to the GC-1 and GC-4 samples. They have lower compressive strength than the 28th day GC-0 sample. On the 90th day, they have higher compressive strength values than the GC-0 sample. A comparison of the strength increase rate of the samples obtained on the 28th and 90th days with the 7th day was calculated. The compressive strength of the mixtures on the 7th day was considered to be 100%. For instance, the compressive strength of the GC-0 sample increased by 15.06% on the 28th day compared to the 7th day. Moreover, it was also decided that the compressive strength of the GC-1, GC-2, GC-3, GC-4 and GC-5 samples increased by 15.93%, 20.21%, 26.97%, 32.62% and 31.17% respectively. The 90th day strength increase of the GC-0, GC-1, GC-2, GC-3, GC-4 and GC-5 samples were 32.15%, 38.18%, 45.32%, 51.22%, 57.92% and 56.35%, in turn. With the increase in the age of the concrete samples, the strength gains were higher in samples containing GC than those without GC. The strength gain rates demonstrate that the GC-5 sample with the lowest compressive strength can reach a higher compressive strength than the GC-0 sample over time.

The physical and chemical structure of cement substitute materials are considered to be important parameters for the strength and durability of concrete in the concrete industry. The fineness of the substitute materials affects the compressive strength of cement-

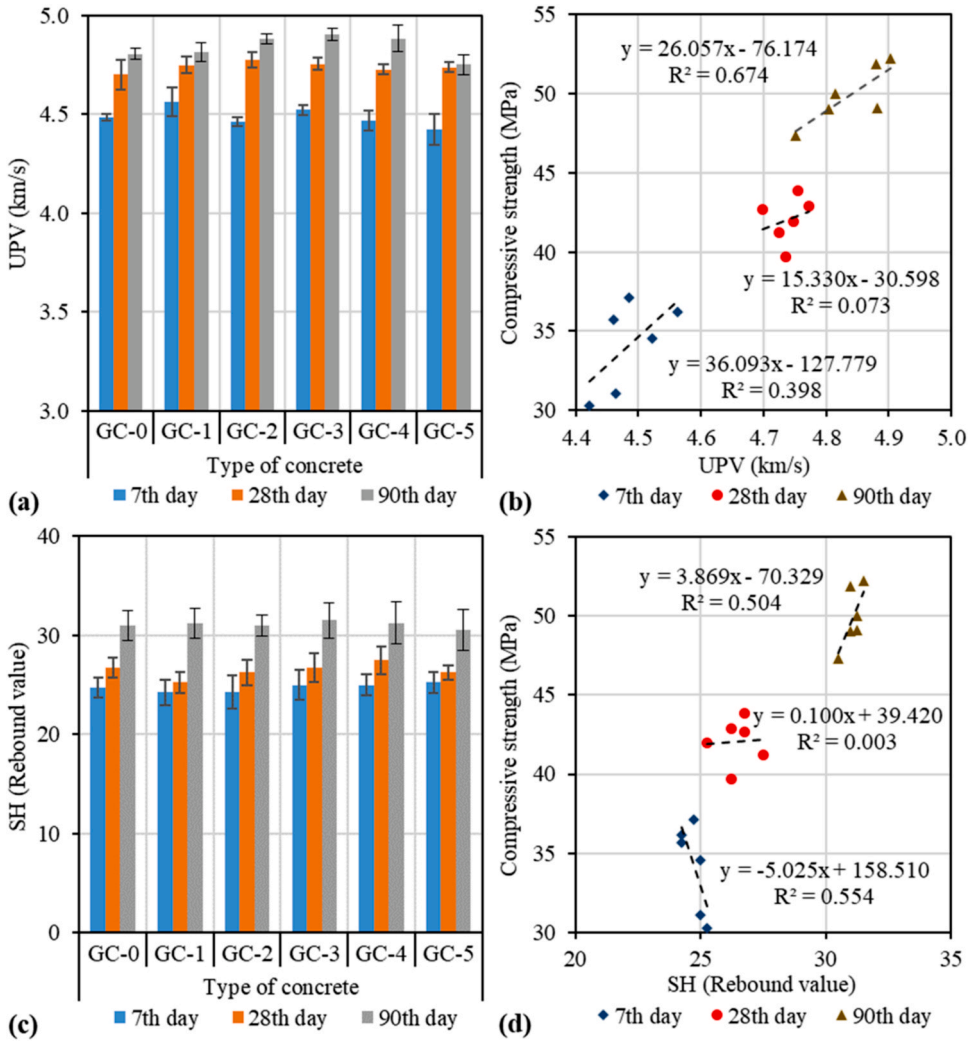

Fig. 9. (a) UPV (b) UPV-Compressive strength relationship (c) SH (d) SH-Compressive strength relationship.

based materials. Usually, as the fineness of a cement substitute material increases, its compressive strength increases. The colemanite fineness values (Blaine) reported in a study examining the effect of colemanite with different physical and chemical properties on the compressive strength of concrete were given to be 3500 cm^2/g, 4000 cm^2/g, and 15,000 cm^2/g. The highest compressive strength in the mortars produced with colemanite with different particle sizes belongs to the colemanite mineral with a fineness of 3500 cm^2/g in the study [32]. Considering the chemical content of these materials, it can be seen that colemanite with a fineness of 3500 cm^2/g has the highest B_2O_3 (40.51%) ratio. This indicates that B_2O_3 in the colemanite structure is effective in increasing compressive strength. It is similar to the physical (Blaine=3432 cm^2/g) and chemical (B_2O_3 =40%) properties of the commercially ground colemanite used in this study. It was found that B_2O_3 increases the compressive strength of hardened concrete, while also affecting fresh concrete by extending its setting time. This situation is similar to the mechanism of the colemanite mineral set retarding additives used in cement-based materials. Set retarding additives used in concrete slow down the hydration mechanism between cement and water. As a result of the hardening of concrete, concrete with set retarding additives attain lower strength values at an early age when compared to plain concrete. Greater strength can be achieved at later ages [52]. The positive effect of colemanite on compressive strength can be explained by its set retarding effect and the spreading of the hydration mechanism over time. Colemanite use in cement-based materials was reported to reduce the hydration temperature and drying shrinkage values [21,33]. As it is known, high hydration temperatures and drying-shrinkage are also crucial causes of crack formation in concrete [53–55]. Additionally, the pozzolanic property of colemanite is mentioned in the literature [14,25,56]. For the natural pozzolan standard, the sum of $SiO_2 + Al_2O_3 + Fe_2O_3$ should be over 70% [57]. However, the colemanite mineral does not meet this requirement. In this respect, it can be said that colemanite is not a pozzolan, but instead acts similarly pozzolan as a mechanism of action.

The flexural, splitting tensile and abrasion test results of concrete samples and the association of compressive strength were given in Fig. 8. According to the 7-day experiment results as in the compressive strength, GC substituted samples have lower flexural and splitting tensile values. Abrasion loss was found to increase with GC substitution. On the 28th and 90th days, the highest flexural and splitting tensile strength values were observed in GC-3 concrete sample. The lowest abrasion loss value at these ages also belongs to the GC-3 concrete sample. Flexural, splitting tensile and abrasion test results were similar to the compressive strength result. When Fig. 8

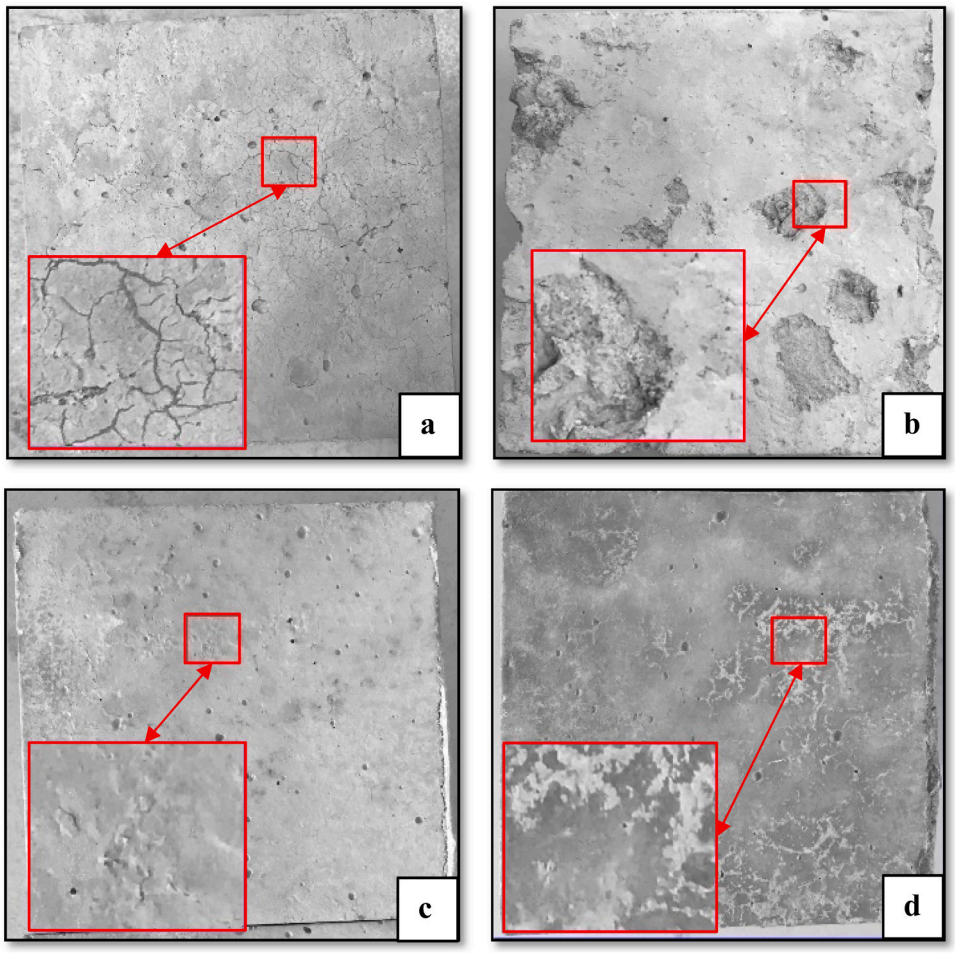

Fig. 10. Visual assessment of samples after (a) wet-dry (b) freeze-thaw (c) sulphate and (d) chloride.

(d) is examined, positive linear correlations between compressive strength and flexural strength (R^2=0.91) as well as compressive strength and split tensile strength (R^2= 0.88) can be found. There is a negative linear correlation between abrasion loss and compressive strength (R^2= 0.95). Therefore, strong linear correlations were detected between test results. In all mechanical tests, the highest strength and the least abrasion were achieved on the 28th day with the GC-3 concrete sample. The lowest strength and highest abrasion were found in the GC-5 sample.

Fig. 9 depicts the UPV and SH rebound values of concrete samples containing GC mineral and the association of these tests with compressive strength. When the UPV and SH data gathered on the 7th and 28th days were analysed, no regular increase or decrease with GC substitution was observed. In other words, the UPV and SH values of the samples on the 7th and 28th days were irregular. The values obtained are not consistent with the GC substitution ratios. This can be explained by the effect of the GC mineral on setting time. UPV and SH measurements of 90-day samples were found to reach significant values with the hardening time of the samples. There was no significant correlation between compressive strength and the UPV and SH tests on the 7th and 28th days. Although precise results cannot be obtained with the UPV and SH tests, they are widely preferred in the evaluation of concrete. Compressive strength results have a high correlation with these tests. When it comes to estimating compressive strength values using the UPV and SH tests, attention should be paid to the data collected especially at the early ages of the concrete samples containing colemanite. It should be noted that reliable data cannot be gathered at an early age with colemanite use. This situation most likely arises due to the hydration process, which spreads over time as a consequence of the retarded setting duration of the concrete.

Briefly, when the destructive and non- destructive tests investigated in this study are evaluated together, the effect of the GC mineral can be generally stated better. GC mineral was effective in increasing the strength and reducing the abrasion of concrete. The best strength and the least abrasion were achieved with 3% GC (GC-3) substitution. This rate differs in some studies in the literature. The reason for this variation may be properties such as the proportion of chemical components in the colemanite mineral, particle size distribution, crystal structure, average crystallite size, and crystal water amount. Moreover, the fact that the colemanite structure and concrete strength is affected by many circumstances such as water/cement ratio, aggregate type, coarse/fine aggregate ratio, concrete compression, curing of concrete may be the reasons for these differences.

3.3. *Effect of raw ground colemanite mineral on durability properties of concrete*

In this study, durability tests were based on penetration of water and harmful solutions into the concrete. Concrete durability is generally related to the penetration and movement of liquids into the concrete [58]. In cement-based materials, water or aggressive liquids can adversely affect the durability. The durability of concrete samples was tested through exposure to wet-dry, freeze-thaw cycles, sulphate and chloride. Post-exposure images of samples exposed to these environments were presented in Fig. 10. It is known that exposure to wet-dry, freeze-thaw, sulphate and chloride impacts the durability performance of concrete [59–61]. The effect of these aggressive environments on durability is mainly the pore structure of the concrete and water penetration into the concrete. Damages on concrete surface vary relative to the environments to which the samples were exposed. The surface damages of the samples exposed to wet-dry and freeze-thaw cycles were observed. Although the damages on the surface of samples exposed to sulphate and chloride were observed visually, they have more undefined shapes than those in other conditions.

Fig. 11 shows mass, UPV and SH losses experienced by concrete samples kept in aggressive environments. As can be seen in Fig. 9, wet-dry exposure, mass, and SH losses of the samples were at a high level, and UPV experienced the least amount of losses. This can be attributed to the deformation of the concrete surface caused by the sudden temperature change during the wet-dry cycle. It is clear that the SH test is affected by the surface properties of the concrete and that small mass losses in concrete start from the surface. Therefore, with the wet-dry cycles, the highest mass losses were seen in SH measurements. The UPV test is generally used to evaluate the internal structure of concrete, and it is obvious that there is an association between mechanical properties [62]. It can be said that with the wet-dry cycle, less damage occurs in the internal structure of concrete than in other environments. Among the concrete samples, GC-3 was the sample least affected by all aggressive environments. When the mechanical properties of concrete samples (Fig. 7) were analysed, the GC-3 sample had higher strength properties than other samples. The fact that the GC-3 sample has low mass, UPV and SH losses was to be expected due to higher strength.

Compressive strength and strength losses of concrete samples exposed to aggressive environments are shown in Fig. 12. Just as in the results of mass loss, it was found that the highest compressive strength losses occur due to the wet-dry cycles. The strength losses of the GC-1, GC-2 and GC-3 samples are less than the GC-0 sample. The GC-4 sample generally has values very close to the GC-0 sample. The GC-5 concrete sample always has the highest strength losses. As a result of the durability tests, the weight and strength of the concrete had decreased. In a previous study, city tap water used in wet-dry and freeze-thaw experiments indicated that higher strength losses would occur if the water in the environment is exposed to concrete with solutions such as sulphate and chloride [63]. The effect of wet-dry and freeze-thaw cycles on the deterioration of concrete strength is a known fact [30,31,63,64]. Besides, as the number of these cycles increases, its effect on concrete also enhances. If wet-dry cycles occur with aggressive liquids, the severity of damage to concrete structures will increase [65]. Water is the cause of damage to samples in durability tests. All the experimental conditions are related to water penetration into the concrete and its movement within it. In the durability tests, the pore structure of concrete samples and the bond strength of cement with aggregate are especially essential. Based on the results of the strength and durability experiments in this study, it was deduced that GC not only increased the strength of concrete but also improved its durability. This is very well matched by the result of a previously reported study [27]: Since the average particle size of GC (d_{50} = 20.683 μm) is close to that of cement (d_{50} = 16.254 μm), the GC strengthens the adherence. A comment can also be made based on the d_{50} value. Because of the low density, the total volume (V_T) of GC substituted for cement in the same amount of mass is high. When the particle shape is assumed to be spherical for the sake of simplicity, it can be said that although the volumes ($V \propto (d_{50})^3$) of the particle are approximately the same,

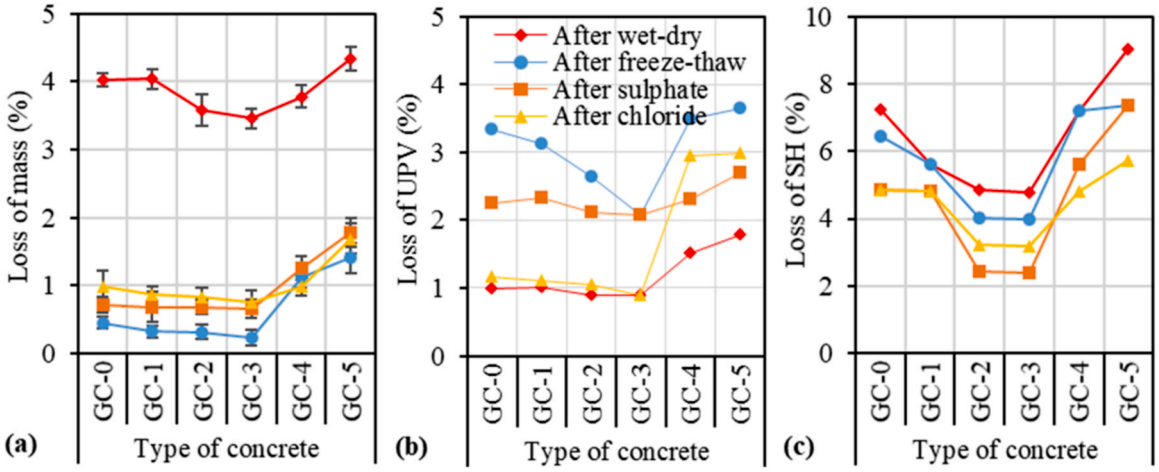

Fig. 11. (a) Mass (b) UPV (c) SH losses of concrete mixtures.

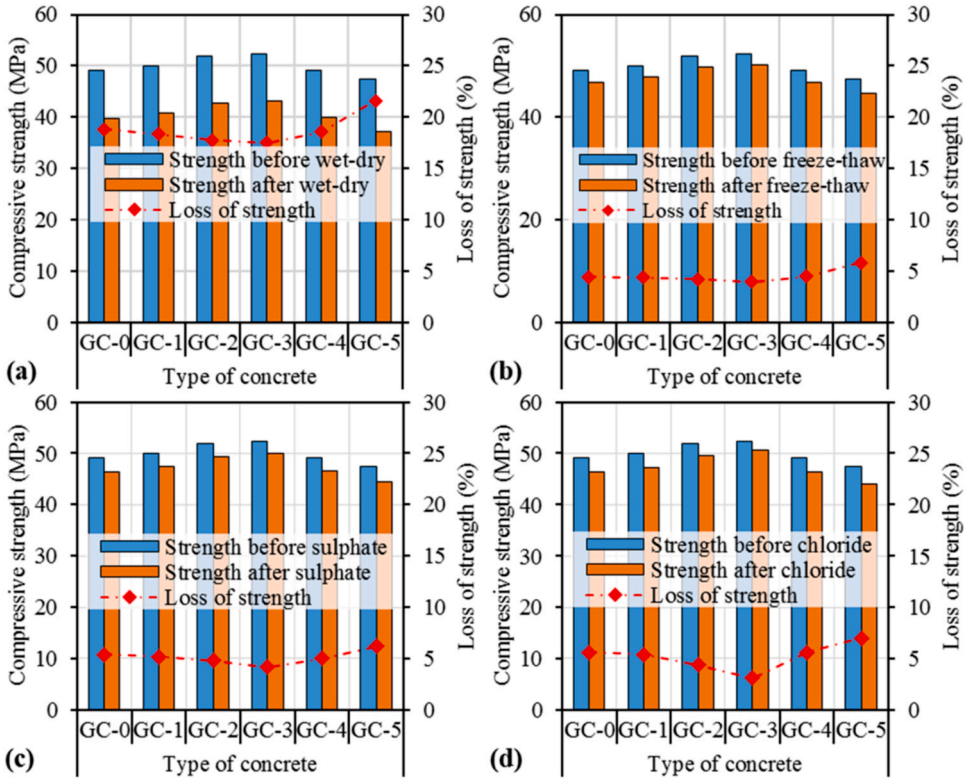

Fig. 12. Compressive strength and strength losses of concrete samples.

the particle number (N) of the GC will increase (Eq. (1)). With the increasing number of particles, the pore will fill more. In conclusion, the adhesion force increases as porosity decreases.

$$V_T = NV = N\frac{4}{3}\pi\left(\frac{d_{50}}{2}\right)^3 \tag{1}$$

4. Conclusions

In this study, the durability (wet-dry, freeze-thaw, sulphate and chloride) of concrete samples produced with raw ground colemanite (GC) mineral substitution was experimentally analysed. The results are as summarized below:

The application of GC mineral substitution up to 5% to cement does not negatively affect the workability of fresh concrete. Depending on the retarded setting and hydration duration, GC substituted mixtures have lower compressive strength, flexural strength, and splitting tensile strength values on the 7th day compared to the control mixture. However, with the increase of concrete age, an increase in the strength values of all GC substituted mixtures was determined. Abrasion resistance, UPV and SH values also confirm the results of strength test. It was observed that the GC mineral is effective in improving strength and abrasion resistance. The GC mineral reached the target strength (C30/37) at all substitution rates. The GC-3 mixture showed the best mechanical properties among the produced concrete. The GC mineral is effective in improving compressive strength as well as concrete durability. It was detected that mixtures produced with GC mineral substitution up to 3% were less damaged than the control mixture in terms of mass loss due to wet-dry, freeze-thaw cycles, sulphate and chloride effects, UPV, SH and compressive strength. In the durability tests, it was observed that the most unfavourable condition causing damage to concrete was the wet-dry cycle. The GC-3 mixture indicated the best durability under aggressive environmental conditions, due to its strength properties. In conclusion, it was seen that raw GC mineral substitution with an average particle size of 12 μm (ranging from 77.851 μm to 335 nm) improves both the strength and durability properties of concrete as adhesion force increases with the particle number.

Funding

The authors have no relevant financial or non-financial interests to disclose.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

Data will be made available on request.

Acknowledgements

The authors would like to thank the Eti Mine Operations General Directorate for supplying the colemanite mineral.

References

[1] J. Ahmad, Z. Zhou, A.F. Deifalla, Self-compacting concrete with partially substitution of waste marble: a review, Int. J. Concr. Struct. Mater. 17 (2023) 1–24, https://doi.org/10.1186/S40069-023-00585-5/FIGURES/20.
[2] Y. Guo, L. Luo, T. Liu, L. Hao, Y. Li, P. Liu, T. Zhu, A review of low-carbon technologies and projects for the global cement industry, J. Environ. Sci. 136 (2024) 682–697, https://doi.org/10.1016/J.JES.2023.01.021.
[3] M.A. Khan, F. Aslam, M.F. Javed, H. Alabduljabbar, A.F. Deifalla, New prediction models for the compressive strength and dry-thermal conductivity of bio-composites using novel machine learning algorithms, J. Clean. Prod. 350 (2022), 131364, https://doi.org/10.1016/J.JCLEPRO.2022.131364.
[4] B.N. AL-Kharabsheh, M. Moafak Arbili, A. Majdi, J. Ahmad, A.F. Deifalla, A. Hakamy, H. Majed Alqawasmeh, Feasibility study on concrete made with substitution of quarry dust: a review, Sustain 14 (2022) 15304, https://doi.org/10.3390/SU142215304.
[5] M.Y. Durgun, A.H. Sevinç, Determination of the effectiveness of various mineral additives against sodium and magnesium sulfate attack in concrete by Taguchi method, J. Build. Eng. 57 (2022), 104849, https://doi.org/10.1016/J.JOBE.2022.104849.
[6] S. Kök, M.S. Türetken, N. Öksüzer, H.S. Gökçe, Effect of elevated temperature on radiation shielding properties of cement and geopolymer mortars including barite aggregate and colemanite powder, Materialia 27 (2023), 101693, https://doi.org/10.1016/J.MTLA.2023.101693.
[7] SBB, 2018. Türkiye Cumhuriyeti Cumhurbaşkanlığı Strateji ve Bütçe Başkanlığı, 11. Kalkınma Planı (2019–2023) Madencilik Politikaları Özel İhtisas raporu, Ankara, Türkiye, 2018.
[8] Eti Maden Refined Products, 2020. ⟨https://www.etimaden.gov.tr/en/chemical-products⟩ (accessed July 20, 2020).
[9] S. Kutuk, Influence of milling parameters on particle size of ulexite material, Powder Technol. 301 (2016) 421–428, https://doi.org/10.1016/j.powtec.2016.06.020.
[10] A.B.D. Nandiyanto, R. Zaen, R. Oktiani, Working volume in high-energy ball-milling process on breakage characteristics and adsorption performance of rice straw ash, Arab. J. Sci. Eng. 43 (2018) 6057–6066, https://doi.org/10.1007/s13369-018-3265-4.
[11] S. Kutuk, T. Kutuk-Sert, Effect of PCA on nanosized ulexite material prepared by mechanical milling, Arab. J. Sci. Eng. 42 (2017) 4801–4809, https://doi.org/10.1007/s13369-017-2643-7.
[12] G. Bumanis, L. Vitola, L. Stipniece, J. Locs, A. Korjakins, D. Bajare, Evaluation of Industrial by-products as pozzolans: A road map for use in concrete production, Case Stud. Constr. Mater. 13 (2020), e00424, https://doi.org/10.1016/j.cscm.2020.e00424.
[13] İ. Ustabaş, A. Kaya, Comparing the pozzolanic activity properties of obsidian to those of fly ash and blast furnace slag, Constr. Build. Mater. 164 (2018) 297–307, https://doi.org/10.1016/j.conbuildmat.2017.12.185.
[14] A. Olgun, T. Kavas, Y. Erdogan, G. Once, Physico-chemical characteristics of chemically activated cement containing boron, Build. Environ. 42 (2007) 2384–2395, https://doi.org/10.1016/j.buildenv.2006.06.003.
[15] Y. Yarar, A. Bayülken, Investigation of neutron shielding efficiency and radioactivity of concrete shields containing colemanite, J. Nucl. Mater. 212–215 (1994) 1720–1723, https://doi.org/10.1016/0022-3115(94)91120-7.
[16] B. Oto, A. Gür, M.R. Kaçal, B. Doğan, A. Arasoglu, Photon attenuation properties of some concretes containing barite and colemanite in different rates, Ann. Nucl. Energy 51 (2013) 120–124, https://doi.org/10.1016/j.anucene.2012.06.033.
[17] D. Demir, G. Keleş, Radiation transmission of concrete including boron waste for 59.54 and 80.99 keV gamma rays, Nucl. Instrum. Methods Phys. Res. Sect. B Beam Interact. Mater. At. 245 (2006) 501–504, https://doi.org/10.1016/j.nimb.2005.11.139.
[18] Boren, Çimento - Bor Araştırma Enstitüsü (BOREN), (2020). ⟨https://www.boren.gov.tr/Sayfa/cimento/36⟩ (Accessed January 18, 2021).
[19] Y. Erdoğan, M.S. Zeybek, A. Demirbas, Cement mixes containing colemanite from concentrator wastes, Cem. Concr. Res. 28 (1998) 605–609, https://doi.org/10.1016/S0008-8846(98)00018-0.

[20] O. Gencel, W. Brostow, C. Ozel, M. Filiz, An investigation on the concrete properties containing colemanite, Acad. J. (2010), https://doi.org/10.5897/IJPS.9000062.
[21] M.A. Glinicki, A. Antolik, M. Gawlicki, Evaluation of compatibility of neutron-shielding boron aggregates with Portland cement in mortar, Constr. Build. Mater. 164 (2018) 731–738, https://doi.org/10.1016/j.conbuildmat.2017.12.228.
[22] K. Okuno, M. Kawai, H. Yamada, Development of novel neutron shielding concrete, in: Nucl. Technol., American Nuclear Society, 2009, pp. 545–552, https://doi.org/10.13182/NT09-A9241.
[23] T. Korkut, A. Ün, F. Demir, A. Karabulut, G. Budak, R. Şahin, M. Oltulu, Neutron dose transmission measurements for several new concrete samples including colemanite, Ann. Nucl. Energy 37 (2010) 996–998, https://doi.org/10.1016/j.anucene.2010.04.005.
[24] M. Kawai, M. Yonemura, T. Kamiyama, K. Okuno, K. Niita, Development of neutron shielding concrete containing colemanite and peridotite, Phys. Soc. Jpn. (2020), 081007, https://doi.org/10.7566/jpscp.28.081007.
[25] O. Aksoğan, H. Binici, E. Ortlek, Durability of concrete made by partial replacement of fine aggregate by colemanite and barite and cement by ashes of corn stalk, wheat straw and sunflower stalk ashes, Constr. Build. Mater. 106 (2016) 253–263, https://doi.org/10.1016/j.conbuildmat.2015.12.102.
[26] M.Y. Durgun, A.H. Sevinç, High temperature resistance of concretes with GGBFS, waste glass powder, and colemanite ore wastes after different cooling conditions, Constr. Build. Mater. 196 (2019) 66–81, https://doi.org/10.1016/j.conbuildmat.2018.11.087.
[27] T. Kutuk-Sert, Stability analyses of submicron-boron mineral prepared by mechanical milling process in concrete roads, Constr. Build. Mater. 121 (2016) 255–264, https://doi.org/10.1016/j.conbuildmat.2016.05.156.
[28] R. Douglas Hooton, Future directions for design, specification, testing, and construction of durable concrete structures, Cem. Concr. Res. 124 (2019), 105827, https://doi.org/10.1016/j.cemconres.2019.105827.
[29] S. Zhang, K. Cao, C. Wang, X. Wang, J. Wang, B. Sun, Effect of silica fume and waste marble powder on the mechanical and durability properties of cellular concrete, Constr. Build. Mater. 241 (2020), 117980, https://doi.org/10.1016/j.conbuildmat.2019.117980.
[30] K.Z. Hanjari, P. Utgenannt, K. Lundgren, Experimental study of the material and bond properties of frost-damaged concrete, Cem. Concr. Res. 41 (2011) 244–254, https://doi.org/10.1016/j.cemconres.2010.11.007.
[31] H. Ma, W. Gong, H. Yu, W. Sun, Durability of concrete subjected to dry-wet cycles in various types of salt lake brines, Constr. Build. Mater. 193 (2018) 286–294, https://doi.org/10.1016/j.conbuildmat.2018.10.211.
[32] M. Ozturk, U.K. Sevim, O. Akgol, E. Unal, M. Karaaslan, Investigation of the mechanic, electromagnetic characteristics and shielding effectiveness of concrete with boron ores and boron containing wastes, Constr. Build. Mater. 252 (2020), 119058, https://doi.org/10.1016/j.conbuildmat.2020.119058.
[33] U.K. Sevim, Colemanite ore waste concrete with low shrinkage and high split tensile strength, Mater. Struct. Constr. 44 (2011) 187–193, https://doi.org/10.1617/s11527-010-9618-4.
[34] S. Kutuk, Öğütülmüş nano boyutlu kolemanit mineralinin elementel ve kristal yapı özellikleri, Erzincan Üniversitesi Fen Bilimleri Enstitüsü Dergisi 10 (2017) 303–313. doi: 10.18185/erzifbed.334656.
[35] I. Waclawska, Thermal behaviour of mechanically amorphized colemanite: II. Internal structure reconstitution processes of ground colemanite, J. Therm. Anal. 48 (1997) 155–161, https://doi.org/10.1007/BF01978975.
[36] I. Waclawska, Thermal behaviour of mechanically amorphized colemanite: I. Thermal decomposition of ground colemanite, J. Therm. Anal. 48 (1997) 145–154, https://doi.org/10.1007/BF01978974.
[37] P. Lotti, D. Comboni, L. Gigli, L. Carlucci, E. Mossini, E. Macerata, M. Mariani, G.D. Gatta, Thermal stability and high-temperature behavior of the natural borate colemanite: an aggregate in radiation-shielding concretes, Constr. Build. Mater. 203 (2019) 679–686, https://doi.org/10.1016/j.conbuildmat.2019.01.123.
[38] Ö. Yildiz, The effect of heat treatment on colemanite processing: a ceramics application, Powder Technol. 142 (2004) 7–12, https://doi.org/10.1016/j.powtec.2004.03.006.
[39] F. Škvára, K. Kolář, J. Novotný, Z. Zadák, The effect of cement particle size distribution upon properties of pastes and mortars with low water-to-cement ratio, Cem. Concr. Res. 11 (1981) 247–255, https://doi.org/10.1016/0008-8846(81)90066-1.
[40] S. Kutuk, T. Kutuk-Sert, An examination of nanoparticle colemanite mineral added warm mix asphalt, Constr. Build. Mater. 243 (2020), 118252, https://doi.org/10.1016/j.conbuildmat.2020.118252.
[41] TS EN 12350–6, 2019. Testing fresh concrete - Part 6: Density, Turkish Standard Institute, Ankara, Turkey, 2019.
[42] TS EN 12350–2, 2019. Testing fresh concrete - Part 2: Slump test, Turkish Standard Institute, Ankara, Turkey, 2019.
[43] TS EN 12350–7, 2019. Testing fresh concrete - Part 7: Air content - Pressure Methods, Turkish Standard Institute, Ankara, Turkey, 2019.
[44] TS EN 12390–5, 2019. Testing hardened concrete - Part 5: Flexural strength of test specimens, Turkish Standard Institute, Ankara, Turkey, 2019.
[45] TS EN 12390–6, 2010. Testing hardened concrete - Part 6: Tensile splitting strength of test specimens, Turkish Standard Institute, Ankara, Turkey, 2010.
[46] TS EN 13892–3, 2015. Methods of test for screed materials - Part 3: Determination of wear resistance - Böhme, Turkish Standard Institute, Ankara, Turkey, 2015.
[47] İ.Bekem Kara, Experimental Investigation of the effect of cold joint on strength and durability of concrete, Arab. J. Sci. Eng. 46 (2021) 10397–10408, https://doi.org/10.1007/S13369-021-05400-5/FIGURES/14.
[48] A. Dehestani, M. Hosseini, A. Taleb Beydokhti, Effect of wetting–drying cycles on mode I and mode II fracture toughness of cement mortar and concrete, Theor. Appl. Fract. Mech. 106 (2020), 102448, https://doi.org/10.1016/J.TAFMEC.2019.102448.
[49] TS EN 1367–1, 2009. Tests for thermal and weathering properties of aggregates - Part 1: Determination of resistance to freezing and thawing, Turkish Standard Institute, Ankara, Turkey, 2009.
[50] U.K. Sevim, M. Ozturk, M.Balcikanli Bankir, U. Aydin, Utilization of colemanite waste in concrete design, Int. J. Adv. Eng. Res. Sci. 4 (2017), https://doi.org/10.22161/ijaers.4.12.25, 2456–1908.
[51] H.G. Ni, J.Z. Wang, Prediction of compressive strength of concrete by neural networks, Cem. Concr. Res. 30 (2000) 1245–1250, https://doi.org/10.1016/S0008-8846(00)00345-8.
[52] P. Tayeb, M. Lullulangi, O. Sampebua, Effect of Retarder Usage on Concrete Characteristic, J. Civ., Constr. Environ. Eng. 4 (2019) 69–72, https://doi.org/10.11648/j.jccee.20190403.12.
[53] A. Mardani-Aghabaglou, M. İlhan, Effect of shrinkage reducing admixture on compressive strength, water absorption and drying-shrinkage of mortar mixture in the presence of water reducing admixture, Sak. Üniversitesi Fen. Bilim. Enstitüsü Derg. 22 (2018) 417–426, https://doi.org/10.16984/saufenbilder.342519.
[54] L. Wang, M. Jin, Y. Wu, Y. Zhou, S. Tang, Hydration, shrinkage, pore structure and fractal dimension of silica fume modified low heat Portland cement-based materials, Constr. Build. Mater. 272 (2021), 121952, https://doi.org/10.1016/j.conbuildmat.2020.121952.
[55] J. Yang, J. Huang, X. He, Y. Su, S.K. Oh, Shrinkage properties and microstructure of high volume ultrafine phosphorous slag blended cement mortars with superabsorbent polymer, J. Build. Eng. 29 (2020), 101121, https://doi.org/10.1016/j.jobe.2019.101121.
[56] I. Kula, A. Olgun, Y. Erdogan, V. Sevinc, Effects of colemanite waste, cool bottom ash, and fly ash on the properties of cement, Cem. Concr. Res. 31 (2001) 491–494, https://doi.org/10.1016/S0008-8846(00)00486-5.
[57] TS 25, 2008. Natural pozzolan (Trass) for use in cement and concrete - Definitions, requirements and conformity criteria, Turkish Standard Institute, Ankara, Turkey, 2008.
[58] C. Wagner, B. Villmann, V. Slowik, V. Mechtcherine, Capillary absorption of cracked strain-hardening cement-based composites, Cem. Concr. Compos. 97 (2019) 239–247, https://doi.org/10.1016/j.cemconcomp.2018.12.017.
[59] J. Zhang, Y. Gao, Y. Han, Interior Humidity of Concrete under Dry-Wet Cycles, J. Mater. Civ. Eng. 24 (2012) 289–298, https://doi.org/10.1061/(ASCE)MT.1943-5533.0000382.
[60] Y. Shen, J. Liu, S. Zhou, G. Li, Experimental investigation on the freeze–thaw durability of concrete under compressive load and with joints, Constr. Build. Mater. 229 (2019), 116893, https://doi.org/10.1016/j.conbuildmat.2019.116893.
[61] S.A. Mangi, M.H. Wan Ibrahim, N. Jamaluddin, M.F. Arshad, R. Putra Jaya, Short-term effects of sulphate and chloride on the concrete containing coal bottom ash as supplementary cementitious material, Eng. Sci. Technol. Int. J. 22 (2019) 515–522, https://doi.org/10.1016/j.jestch.2018.09.001.

[62] İ.Bekem Kara, M. Arslan, Effects of plasticizer and antifreeze on concrete at elevated temperatures and different cooling regimes, Rev. La Constr. 19 (2020) 347–357, https://doi.org/10.7764/RDLC.19.3.347.
[63] J. Tang, H. Cheng, Q. Zhang, W. Chen, Q. Li, Development of properties and microstructure of concrete with coral reef sand under sulphate attack and drying-wetting cycles, Constr. Build. Mater. 165 (2018) 647–654, https://doi.org/10.1016/j.conbuildmat.2018.01.085.
[64] W.L. Qiu, F. Teng, S.S. Pan, Damage constitutive model of concrete under repeated load after seawater freeze-thaw cycles, Constr. Build. Mater. 236 (2020), 117560, https://doi.org/10.1016/j.conbuildmat.2019.117560.
[65] K. Li, C. Li, Z. Chen, Influential depth of moisture transport in concrete subject to drying-wetting cycles, Cem. Concr. Compos. 31 (2009) 693–698, https://doi.org/10.1016/j.cemconcomp.2009.08.006.