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Effect of Colemanite-Based Boron Concentrator Waste on Concrete Properties

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Keywords

Colemanite waste,
Boron,
Fly ash,
Concrete,
Mechanical properties.

Abstract

It is estimated that approximately 0.5-1 million tons of boron waste is generated annually in Turkey. Most of these wastes are concentrated in Kırka (Eskişehir), Bandırma (Balıkesir) and Bigadiç (Balıkesir) plants. Disposal of these wastes is an important environmental problem. In this study, the usability of colemanite concentrator waste from Kütahya-Emet Eti Maden Company as cement and concrete admixture was investigated by experiments on concrete specimens. The strengths of colemanite concentrator waste at 5%, 10%, 20% and by changing the proportions of colemanite concentrator waste and adding fly ash with the waste into cement at 10% and 20% were investigated. When the mechanical properties were examined, 5% colemanite waste gave the best results in the specimens. It was also observed that it reduced the setting time.

1. Introduction

Boron is a rare element that is not found in free form in nature and is present in the structure of more than 250 minerals and is used in many fields such as glass, ceramics, cleaning, agriculture, metallurgy and nuclear industry [1-2]. Although Turkey has approximately 72.2% of the world boron reserves, it is not at a sufficient level in the production and trade of boron products and refined boron compounds [3]. As a result of the physical enrichment methods used during boron mining, boron-containing wastes are generated and failure to utilise these wastes leads to economic losses, environmental pollution and storage problems [4]. Colemanite and tincal concentrator wastes have similar chemical composition with mineral additives used in cement production and show pozzolanic properties that increase the durability and binding of concrete [5]. The utilisation of these wastes in cement and concrete production contributes both to the reduction of environmental problems and economic gain [6]. Economically important boron minerals are found in hydrated forms with calcium, sodium and magnesium compounds. The main boron minerals of commercial value include tincal (borax), kernite, urexite, colemanite and sasolite. While borax dissolves easily in water, kernite dissolves more slowly and colemanite has very low solubility in water. Ulexite is called 'cotton rose' due to its white and slightly transparent appearance, while sasolite crystallises in the triclinic system and forms white and bright crystals. Boron and boron oxide (B_2O_3) contents of these minerals are variable, and boron compounds have important usage areas in industry and technology [7-9]. With the concentration of boron reserves in certain regions and the increasing importance of boron in technology, the use of boron has increased greatly in recent years. However, the lack of scientific research on boron in the past and the lack of utilization of industrial wastes generated during boron processing have limited the usage areas of these wastes. The construction sector was also affected by this situation and boron wastes were not used in cement or concrete [10]. Recent research has revealed some important properties of boron wastes, especially it has been determined that boron-containing cements reduce the radiation permeability and prolonged the setting time. These findings indicate that boron wastes can be used as artificial pozzolan in

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concrete [11]. Boron products are widely used in the construction industry and provide advantages such as protection against decay and staining, pest resistance, water resistance, flame retardancy, heat and sound insulation. The use of B_2O_3 additive in cement production saves energy by reducing the baking temperature and prolonged the setting time. In addition, boron-containing construction materials are widely used in roof coatings and cellulosic insulation systems. In particular, boron-added cellulosic insulation materials find an important area of use in wooden structures due to their low cost and ease of application [12].

Studies with boron-activated belite cement (BAB) have shown that it increases the durability of concrete and significantly improves its impermeability to water and chemicals. While the durability of concrete increases as the water/cement ratio decreases, it has been determined that concretes produced with BAB cement provide higher durability and low permeability even at lower dosages compared to normal Portland cement [13]. In Turkey, the National Boron Research Institute (Boren) has been supporting the development of boron activated belite cement, and studies have focused on investigating the mechanical properties of cements enriched with boron minerals such as colemanite and ulexite [14]. In experiments, it was found that boron cement admixtures prolonged setting times, increased compressive strength and showed resistance of concrete to water and chemicals, especially at low dosages [15]. In addition, it has been observed that cements containing borogypsum and colemanite concentrator wastes increase strength when used at certain ratios but cause a decrease above a certain ratio. In general, it has been demonstrated that boron-added cement provides advantages especially in terms of impermeability and durability of concrete, thus material saving and performance improvement can be achieved in cement production [16]. While the composition and hydration processes of normal Portland cement are explained, it is stated that thermal cracks that may occur with the use of BAB cement especially in mass concrete can be prevented. It is emphasised that B_2O_3 reduces the clinkerisation temperature in cement production and is used as a plasticiser in the glass industry, while it is stated that the chemical resistance of cements containing B_2O_3 is high [17-18]. In the recent studies, different aspects of the usability of boron waste in sustainable binder systems were investigated. In the studies conducted on alkali-activated mortars containing boron waste, volcanic scoria and granulated blast-furnace slag, it was observed that the inclusion of boron waste in the mixtures negatively affected the compressive strength and durability properties, and the best performance at 100 °C was obtained with a mixture of 50% blast-furnace slag and 50% volcanic scoria [19]. In one-component geopolymer binders prepared by the alkaline fusion method using boron waste from Kırka, the optimum compressive strength was obtained at 650 °C with 4% NaOH, while higher temperatures decreased the strength [20]. Furthermore, the inclusion of up to 20% tincal-based waste in geopolymeric mortars resulted in good mechanical performance before and after high temperatures and a strong correlation between compressive strength and ultrasonic pulse velocity [21]. These studies indicate that boron waste can be considered as a potential binder component in geopolymer technology when used in limited proportions. In this study, it was investigated whether Kütahya-Emet colemanite concentrator waste improves the properties of cement paste and concrete samples, and the usability of this waste as concrete and cement admixture was examined by experiments. Although there have been many studies on the use of boron waste in concrete technology, colemanite concentrator waste has not been studied in concrete. Its chemical composition and physical properties were evaluated and its effects on concrete were analysed and the potential usage areas of this material were determined with the results obtained. Thus, it is aimed to utilize colemanite concentrator waste as an industrial value, prevent environmental pollution and contribute to the national economy.

2. Experimental Study

2.1. Materials

CEM I 42.5 R type cement was used in concrete production. Boron waste was taken from Eti Maden (Kütahya) Emet Boron Factory established in Emet boron deposits. Fly ash is Seyit Ömer thermal power plant fly ash and was obtained from Kütahya Cement Company. The properties of cement, fly ash and boron waste are given in Table 1. 0-4 mm sand and 4-31.5 mm crushed stone with specific gravities of 2.56 and 2.73 respectively were used as aggregates in the study. Tap water was used as mixing water.

Table 1. Properties of cement, fly ash and boron waste

	Chemical Content, %							Physical Properties	
	SiO_2	CaO	Al_2O_3	MgO	SO_3	Fe_2O_3	B_2O_3	Specific Weight	Blain, cm^2/gr
Cement	18.99	63.8	4.36	1.19	2.73	2.83	-	3.06	3644
Fly ash	53.69	3.4	20.29	4.09	0.99	-	-	1.98	4020
Boron Waste	21.89	18.13	2.26	6.65	-	1.19	27.80	2.42	-

2.2. Method and tests

Concrete mixes were obtained using the mix proportions given in Table 2. In the mixes, boron waste was used in the proportions of 5, 10, 20% instead of cement. In addition, 10%, 10%, 20% fly ash was used instead of cement in the 10% boron waste mixes and 10% fly ash was used instead of cement in the 20% boron waste mixes.

Table 2. Concrete mix proportions, kg/m^3

	C	C5B	C10B	C20B	C10B10FA	C10B20FA	C20B10FA
Cement	300	285	270	240	240	210	210
Boron waste	0	15	30	60	30	30	60
Fly ash	0	0	0	0	30	60	30
Water	175	175	175	175	175	175	175
Crushed stone	1127	1127	1127	1127	1127	1127	1127
Sand	864	864	864	864	864	864	864

A slump test was performed on each mix from the fresh concrete tests. A minimum of three 15 cm cube specimens were taken from each mix for each test. After 1 day, the specimens were removed from the mold and kept under standard curing conditions until the day of testing. Unit weight, ultrasonic pulse and compression tests were carried out on 28 day old specimens as hardened concrete tests. Unit weight is determined by dividing the weight by the total volume. The ultrasonic pulse velocity is obtained by dividing the sample length by the time it takes for the vibration generated by the transmitting probe to reach the receiving probe in the specimen. Compressive strength is obtained by dividing the compressive force by the specimen area. Images of the concrete mix, the specimens in the mold and the slump, ultrasonic pulse and compression tests are given in Figure 1.

Figure 1. Dry mixtures, specimens, fresh and hardened tests of concrete

3. Results and Discussion

Slump values of fresh concrete mixes are shown in Figure 2. Analysis of Figure 2 shows that the slump values increase by up to 25% as the amount of colemanite concentrator waste added to the concrete mix in place of cement increases. The reason for this may be that colemanite concentrator waste does not agglomerate in the mix, thus improving flowability and workability.

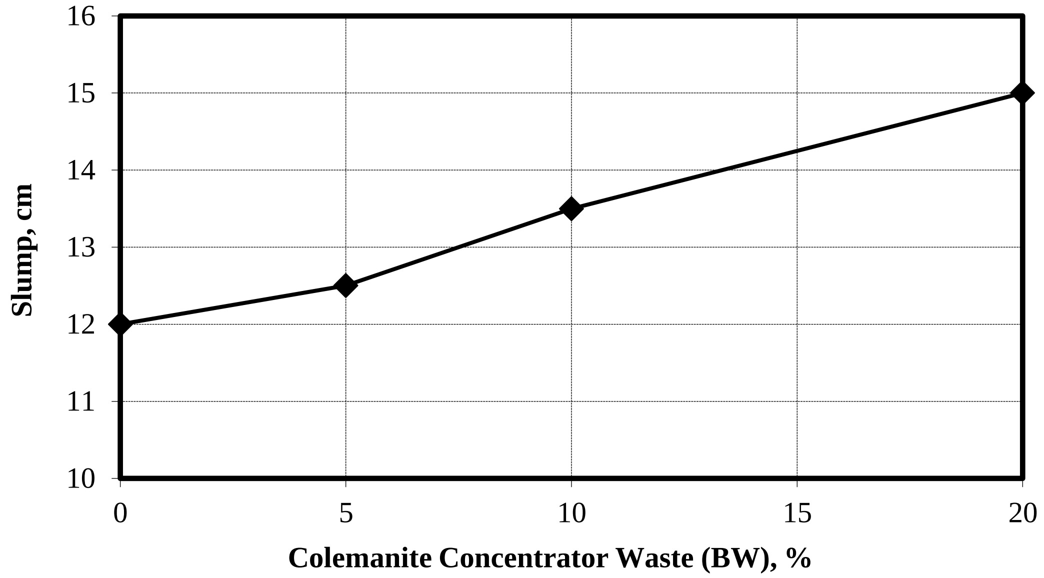

Figure 2. Variation of slump in fresh concrete due to increase in colemanite concentrator waste

The slump values of the fresh concrete mixes were formed as shown in Figure 3 when the colemanite concentrator waste and fly ash, which are wastes generated during boron extraction, were used instead of cement. Analysis of Figure 3 shows that the slump values increased by up to 33% as the proportion of colemanite concentrator waste and fly ash added to the concrete mix in place of cement increased. In addition to improving the workability of this boron based waste, it was observed that fly ash also improved the workability. The reason for this is that, unlike other mineral admixtures, fly ash has a more rounded structure and, thanks to this rounded structure, it can partially increase the fluidity with rotational movement during concrete casting. It can be said that this phenomenon, also known as the lubrication effect, increases the workability.

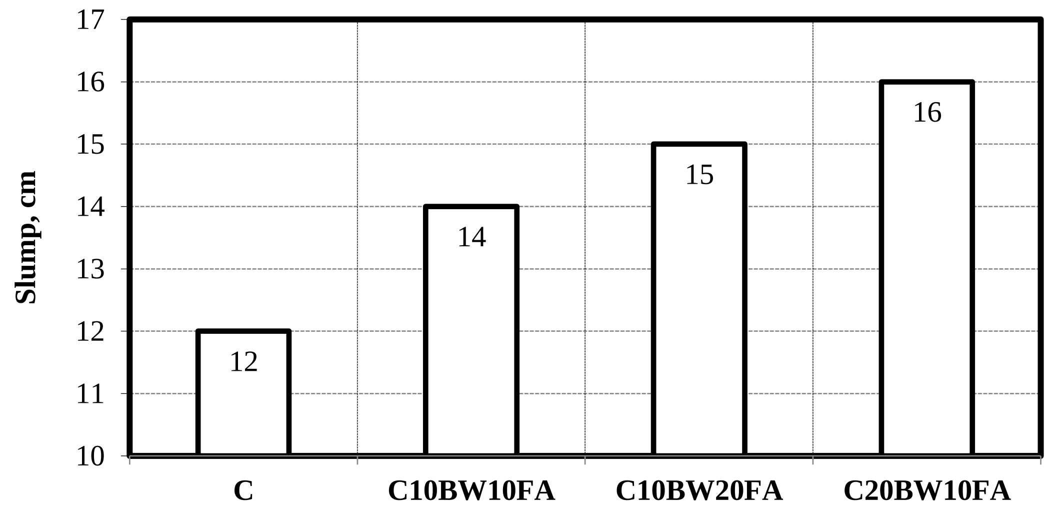

Figure 3. Variation of fresh concrete slump as a function of colemanite concentrator waste and fly ash content

Figure 4 shows the change in concrete unit weight as a function of the proportion of colemanite concentrator waste added to the mix in place of cement. When analysing Figure 4, the hardened concrete unit weight values increased by up to 5% as the ratio of colemanite concentrator waste increased. The density of colemanite concentrator waste added in place of cement is lower than the density of cement. Therefore, a decrease in concrete unit weight is expected. However, the increase in workability caused the concrete to settle better, the voids formed as a result of compaction decreased and therefore the unit weight increased due to the increase in filling ability.

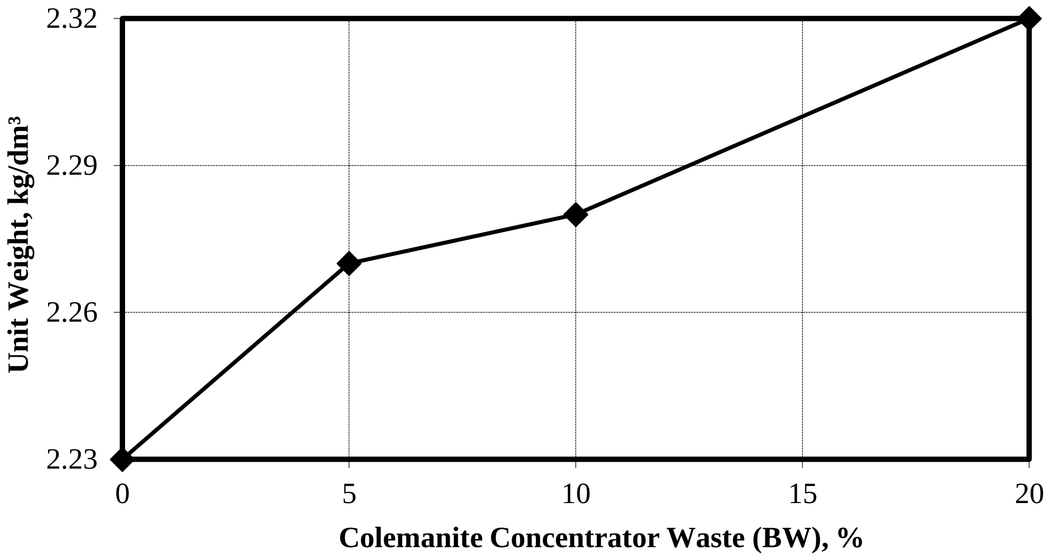

Figure 4. Variation of concrete unit weight as a function of increase in colemanite concentrator waste ratio

The changes in the unit weights of the hardened concrete when fly ash is used instead of cement, together with the condenser waste generated during the extraction of colemanite, a boron compound, are shown in Figure 5. When analysing the data in Figure 5, it can be seen that the lowest unit weight value belongs to the control concrete (C) with 2.23 g/cm³. An increase in the unit weight values is observed in the concrete specimens containing colemanite condenser waste and fly ash. C10BW10FA specimen was 2.28 g/cm³, C10BW20FA specimen was 2.30 g/cm³ and the highest unit weight value was measured in C20BW10FA specimen with 2.32 g/cm³. These results show that the addition of colemanite condenser waste and fly ash has an increasing effect on the density of concrete. One of the reasons for this increase may be that colemanite condenser waste and fly ash, together with cement, have binding properties and form a denser structure. In addition, these admixtures may have contributed to the increase in unit weight by better filling the voids in the concrete and reducing porosity. In particular, the silica content of colemanite condenser waste may also explain this situation by promoting hydration reactions and forming a denser microstructure.

Figure 6 shows the change in concrete ultrasonic pulse velocity as a function of the proportion of colemanite concentrator waste added to the mix in place of cement. According to the data in Figure 6, as the amount of colemanite condensate waste increases, the ultrasonic pulse velocity also increases. While the lowest ultrasonic pulse velocity measured in the control concrete was 2.92 km/h, this value increased to 3.25 km/h in the 10% colemanite sample and to 3.31 km/h in the 20% colemanite sample. One of the main reasons for this increase is that the colemanite condenser waste contributes to the cement matrix, improves the concrete microstructure and reduces the internal void ratio. The positive effect of colemanite waste on the hydration process results in a denser and more durable structure, which allows faster propagation of ultrasonic waves. Other possible reasons for the increase in ultrasonic pulse velocity are the increase in continuity of the internal structure of the concrete and the decrease in microcracking with increasing colemanite content.

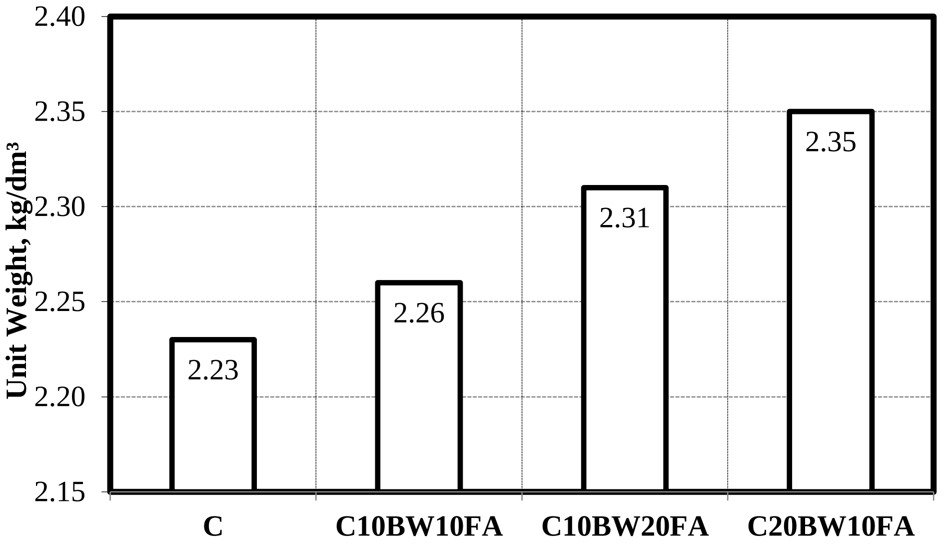

Figure 5. Varying concrete unit weight depending on colemanite concentrator waste and fly ash content

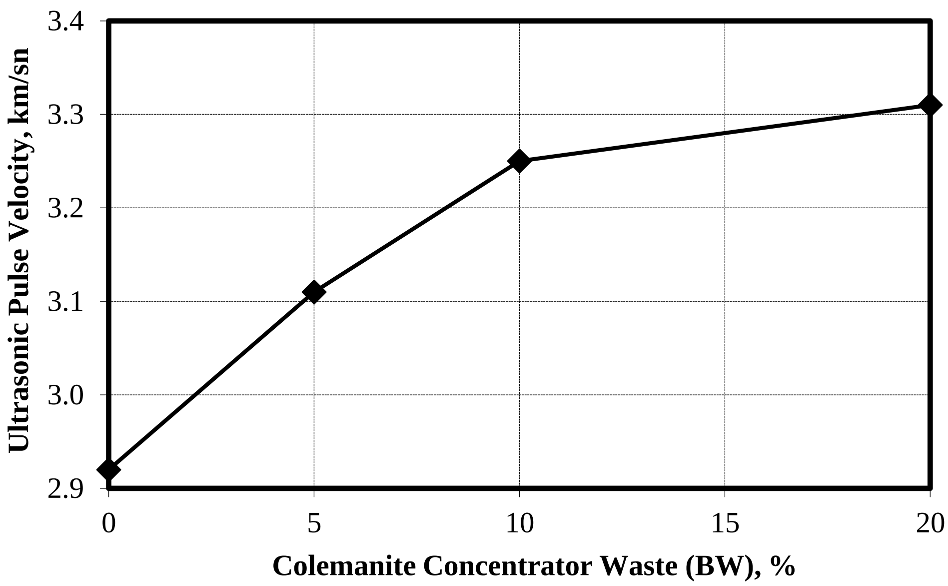

Figure 6. Variation of ultrasonic pulse velocity depending on the increase of colemanite concentrator waste

The changes in the ultrasonic pulse velocity of the hardened concrete when fly ash is used instead of cement, together with the condenser waste generated during the extraction of colemanite, a boron compound, are shown in Figure 7. From the data in Figure 7, it can be seen that as the use of colemanite condenser waste and fly ash in concrete mixes increases, so do the ultrasonic pulse velocities. The control concrete (C) had the lowest ultrasonic pulse velocity and was measured to be 2.92 km/sec. This value increased to 3.05 km/sec in the C10BW10FA sample which contained 10% colemanite condenser waste and 10% fly ash instead of cement. In the C10BW20FA sample, where the colemanite content was kept constant and the fly ash content was increased to 20%, the ultrasonic pulse velocity reached 3.29 km/sec, while the highest value of 3.37 km/sec was measured in the C20BW10FA sample, where the colemanite content was increased to 20%. The main reason for this increase is that colemanite condenser waste and fly ash tighten the internal structure of the concrete, reduce the void ratio and improve the microstructure. In particular, colemanite promotes hydration reactions and increases bonding, creating a denser structure and allowing ultrasonic waves to propagate faster in the concrete. In addition, the additives that fill microcracks and increase the internal continuity of the structure may also have contributed to the increase in the ultrasonic pulse velocity.

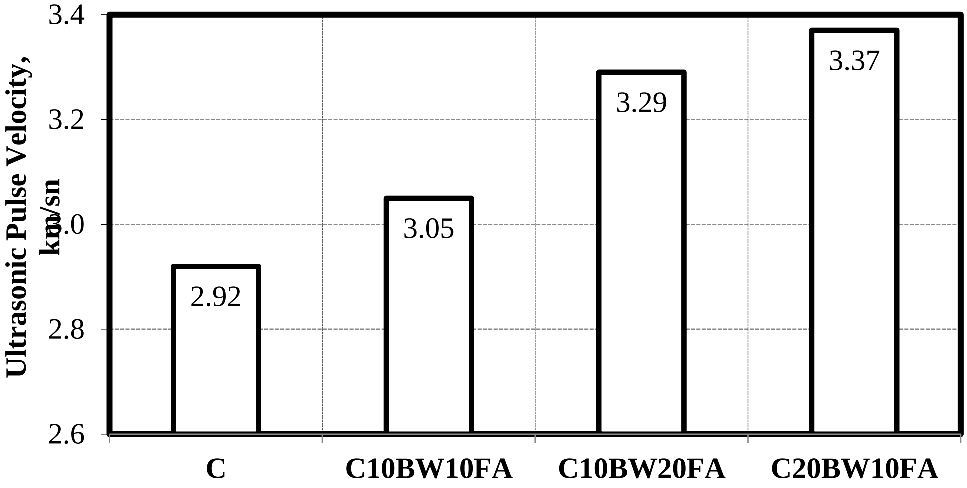

Figure 7. Ultrasonic pulse velocities of concretes containing colemanite concentrator waste and fly ash

Figure 8 shows the change in concrete compressive strength as a function of the proportion of colemanite concentrator waste added to the mix in place of cement. From the compressive strength results obtained, it can be seen that the addition of colemanite condenser waste has different effects on the mechanical performance of the concrete. The control concrete (C) was taken as the reference with a compressive strength of 48.20 MPa. In specimen C5B, where 5% colemanite condenser waste was used instead of cement, the strength increased to 49.57 MPa, the highest value, similar to the literature [22]. However, the compressive strength decreased to 43.62 MPa in specimen C10B where the colemanite content was increased to 10%, while the lowest value of 30.12 MPa was measured in specimen C20B containing 20% colemanite. The use of small amounts (5%) of colemanite waste improved the microstructure of the concrete by supporting the binding properties and increasing the strength. However, as the amount of cement decreased with increasing colemanite content, the binder phase weakened and the strength decreased. In particular, in the sample containing 20% colemanite, the replacement of cement by a large proportion of colemanite waste prevented the formation of sufficient bond and caused a loss of strength. These results indicate that colemanite waste should be used at an optimum level and that excessive addition of colemanite waste may adversely affect the mechanical performance of concrete.

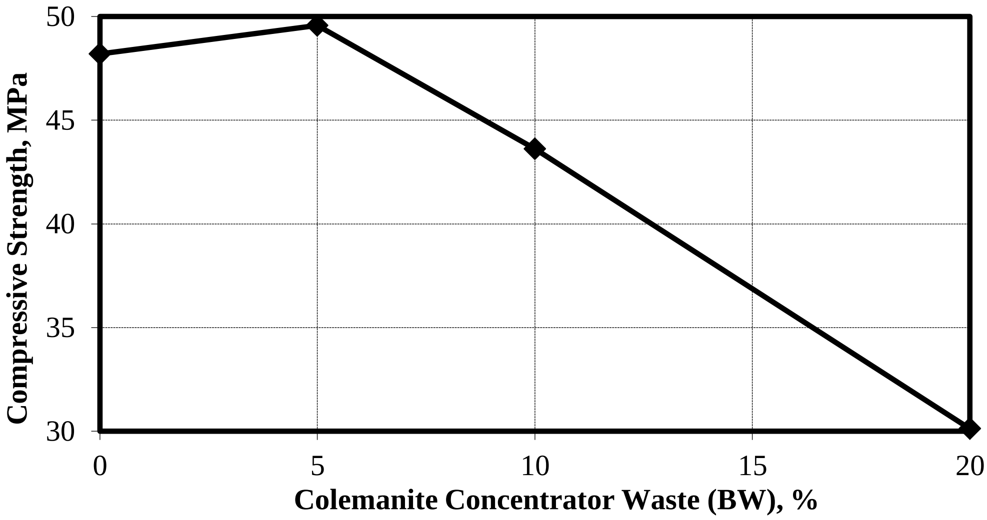

Figure 8. Compressive strength variation of concrete depending on colemanite concentrate content

The changes in the compressive strength of the hardened concrete when fly ash is used instead of cement, together with the condenser waste generated during the extraction of colemanite, a boron compound, are shown in Figure 9. From the compressive strength results obtained, it can be seen that the mechanical strength of the concrete decreases as the colemanite condenser waste and fly ash contents increase. The control concrete (C) shows the highest value with a compressive strength of 48.20 MPa. The compressive strength of C10BW10FA, which contains 10% colemanite condenser waste and 10% fly ash instead of cement, decreased to 45.45 MPa, while the strength of C10BW20FA, in which the fly ash content was increased to 20%, was measured to be 41.99 MPa. The lowest compressive strength of 33.16 MPa was obtained in the C20BW10FA specimen where the colemanite content was increased to 20%. These results indicate that the use of colemanite condenser waste and fly ash in certain proportions may have a negative effect on concrete strength. The decrease in the binding strength of cement may have caused the loss of strength due to the lower binding properties of colemanite and fly ash compared to cement. In addition, the slowing down of the initial hydration reactions and the weakening of the binder phase with increasing fly ash content can be considered as another reason for the decrease in strength. However, it should also be considered that such admixtures can have positive effects on the durability of concrete in the long term.

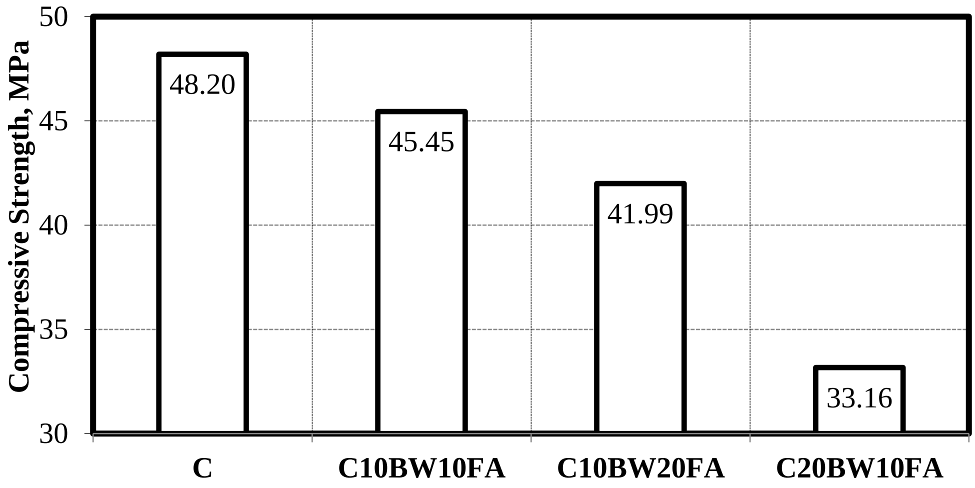

Figure 9. Compressive strengths of specimens containing colemanite concentrator waste and fly ash

4. Conclusions

The conclusions of the study are summarized as follows:

- The addition of colemanite concentrator waste and fly ash increased the workability of fresh concrete mixes, with slump values rising up to 25% and 33%, respectively. This is attributed to the non-agglomerating nature of colemanite waste and the lubrication effect of fly ash.
- The unit weight of hardened concrete increased with the incorporation of colemanite concentrator waste and fly ash. The control concrete had the lowest unit weight (2.23 g/cm³), while the highest value (2.32 g/cm³) was observed in the C20BW10FA specimen. This is due to improved compaction, reduced voids, and enhanced filling ability of these materials.
- Ultrasonic pulse velocity values increased with the addition of colemanite concentrator waste and fly ash. The control concrete had the lowest velocity (2.92 km/sec), while the highest (3.37 km/sec) was recorded in C20BW10FA. This improvement is due to the densification of the microstructure, reduced internal voids, and enhanced hydration reactions.
- The compressive strength results indicate that low amounts of colemanite waste (5%) improved concrete strength (49.57 MPa), but higher replacement levels led to a decline in strength (30.12 MPa at 20%

replacement). The reduction in binding properties and weakening of the binder phase contributed to this decrease.

- Similarly, the combination of colemanite concentrator waste and fly ash reduced compressive strength. The control concrete had the highest strength (48.20 MPa), while the lowest (33.16 MPa) was observed in C20BW10FA. The decrease is attributed to the reduction in cementitious material, slower hydration reactions, and a weaker binder phase.

Overall, the use of colemanite concentrator waste and fly ash can enhance workability, density, and microstructural integrity but may negatively impact compressive strength at high replacement levels. Therefore, optimizing their proportions is crucial to balancing strength and durability in concrete applications. As a result of the study, it is recommended to use 5% colemanite concentrator waste. It is also recommended to investigate the effect of this waste on durability for future studies.

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Declaration of Competing Interest

No conflict of interest was declared by the authors.

Authorship Contribution Statement

Serdal Ünal: Methodology, Data Preparation, Writing, Reviewing
Mehmet Canbaz: Supervision, Writing, Reviewing and Editing

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