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Research article

Geological evaluation of black shale as a suitable Supplementary Cementitious Material (SCM) to optimize the use of clinker in cement production

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ABSTRACT

Faced with challenges like resource depletion and climate change, the cement industry needs sustainable solutions. This study explores the potential of geologically-delinaeated black shale from Apersua, Ghana, as a supplementary cementitious material (SCM) to reduce reliance on traditional methods. The researchers analysed the shale's chemical composition and mineralogy, then created laboratory cement formulations with varying black shale content. These were compared to standard formulations without shale. The results show cement with black shale has comparable compressive strength, meeting standard requirements. Even a formulation with only black shale (excluding limestone, a common ingredient) passed strength tests. Overall, the black shale demonstrated good potential as a SCM based on strength, chemical makeup, setting time, and its possible contribution to durability. This research suggests that black shales from Apersua are worth exploring further as a sustainable and potentially cost-effective alternative in cement production.

1. Introduction

Cement (a hydraulic binder), a fine-grained inorganic material, is a vital element in modern construction. When mixed with water, it forms a paste that hardens through hydration, maintaining strength and stability even underwater [1]. Its long history and widespread use are testaments to its importance. Despite its significance, the cement industry grapples with several challenges of rising costs of raw materials, energy resources, and the ever-growing concern over CO_2 emissions [2,3]. In addition, factors like potential green taxes and penalties for unrestricted emissions are predicted to cause a significant rise in cement prices, possibly doubling by 2030 [4]. For example, the prices and environmental impact of clinker keep rising, and this key raw material constitute at least 60 % of

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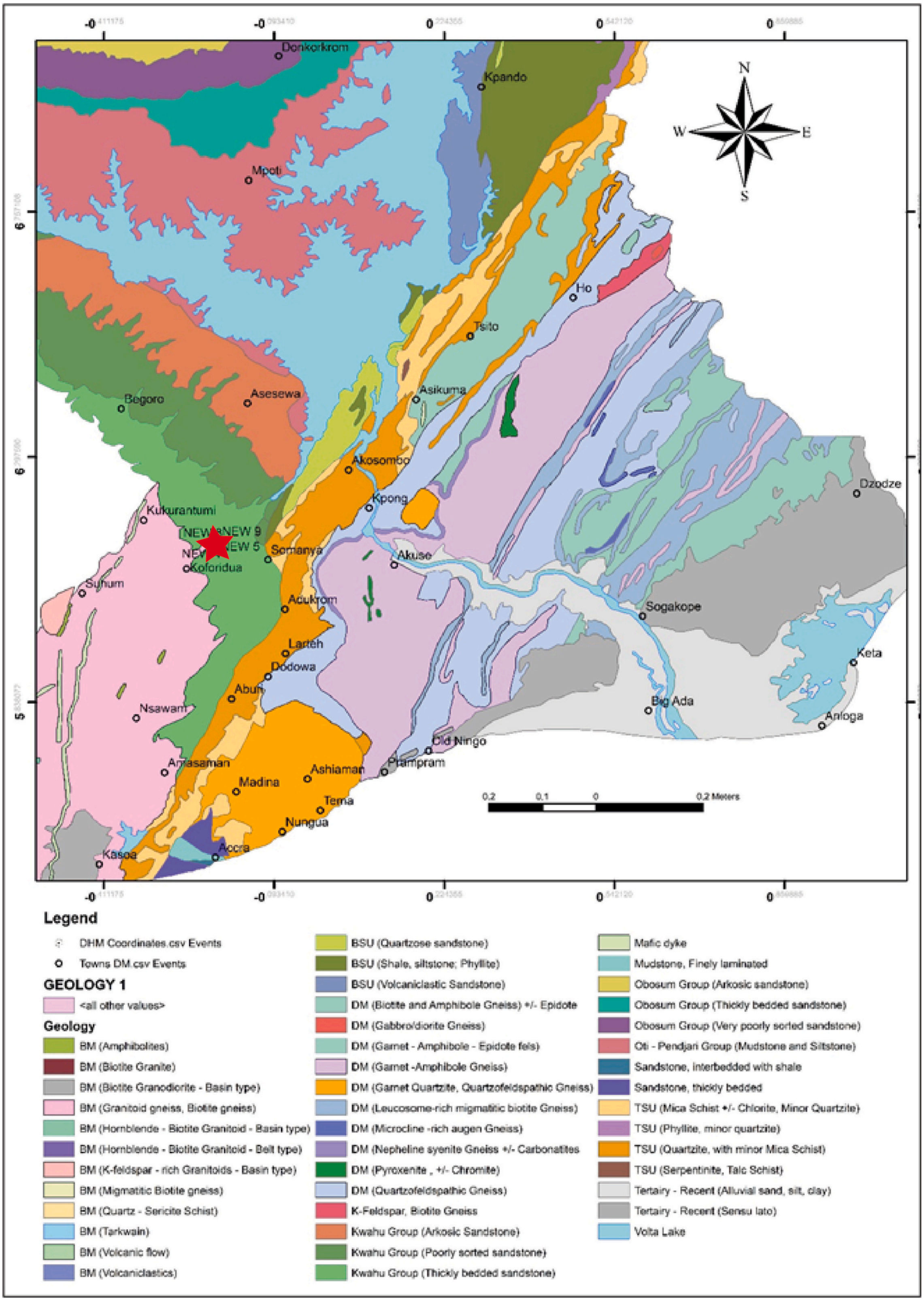

Fig. 1. Simplified geological map of Neoproterozoic Voltaian Basin and the Pan-African Mobile belt. The sampled area marked by the red star within the Apersua vicinity and forms part of the Kwahu Group representing the Lower Voltaian megasequence.

the Ordinary Portland Cement (OPC) manufacture in Ghana [5,6]. These challenges necessitate the exploration of alternative materials. For instance, one of the most effective strategies to lessen this environmental impact involves replacing clinker with supplementary cementitious materials (SCMs) [7]. The addition of SCMs to blended cements triggers various reactions, influenced by their physical (especially specific surface area) and chemical/mineralogical composition [8]. SCMs in the form of chemical admixtures has emerged as a widely accepted solution for improving the performance of low-clinker cements and concrete [5,9,10].

Recent years have seen a surge in research on supplementary cementitious materials (SCMs) [11–13]. This growing interest stems from two key factors of SCMs (i) partially replacing clinker, the most energy-intensive component of cement [14], and (ii) the vast range of readily available materials suitable for use as SCMs. These SCMs are typically soluble powders rich in silica and calcium aluminosilicates [13]. They can be partially incorporated into the clinker during cement production or partially substitute Portland cement in concrete mixes [14]. Notably, SCMs exhibit either pozzolanic or hydraulic behaviour. This means they can harden underwater and form cementitious products through hydration reactions [15]. The vast array of SCMs can be categorized into natural and artificial based on their origin [15,16]. The earlier type is utilized in their natural state as SCM, and may include pyroclastic rocks (formed from volcanic eruptions) and highly siliceous sedimentary rocks like diatomaceous earths. The artificial type often requires processing to modify their structure before being used as SCMs. They can take various forms, including blast furnace slag, silica fume, and fly ash. A further sub-division can be based on the industrial processes used in their production or the original materials that are thermally treated to create them.

As a way of seeking solution to clinker availability issues coupled with its environment implications, especially in Ghana, this research explores rocks that could supplement the fraction of clinker demand within the Ghanaian cement industry as a potential SCM. Thus, the shale rocks delineated within the Apersua vicinity (Fig. 1) in the Eastern Region of Ghana have been explored and examined as a potential SCM.

2. Study area and geology

Apersua, a small town situated in Ghana's Eastern Region near Somanya (Fig. 1) and geologically, lies within the Neoproterozoic Voltaian Basin of Ghana, specifically, the Kwahu Group (Fig. 1) or Kwahu-Bombouaka Group. The Late Mesoproterozoic era (approximately 1100–993 million years ago), Kwahu-Bombouaka Group is dominated by sandstones at its base, with a lesser presence of argillaceous shales towards the top [17,18]. The Voltaian Basin itself is a vast inland sedimentary basin encompassing roughly one-third of Ghana's landmass, with an estimated area of 103,600 square kilometers [19,20]. Geologically similar to the Taoudeni Basin, it reaches an estimated depth of 5–7 km and is comprised of three major stratigraphic divisions, thus, from bottom to top, namely the Kwahu-Bombouaka, Oti-Pendjari, and Tamale-Obosum Groups [17,21–24]. These groups, further subdivided into formations and members with varying lithofacies, often receive names based on their type localities [24]. Therefore, the shaly rocks found near Apersua belong to the Lower Voltaian rocks of Ghana, specifically the Kwahu-Bombouaka Group.

3. Materials and method

This study adopted reliable methods within the scientific community that have standard procedures in the scope of engineering geology, cement production, and laboratory analytical works, especially for rock microscopy, mineral and elemental analysis. Thin section petrographic studies, and X-ray Diffraction (XRD) analysis were carried out at the Department of Earth Science, and Physics, all at the University Ghana.

For other relevant physico-chemical tests related to cement production, and X-ray fluorescence (XRF) spectroscopy analysis were carried out using the laboratory facilities of CBI Ghana Limited. A simplified flowchart summarizing the research process is presented in Fig. 3. The results obtained from these methods will be detailed in the subsequent sections. The XRF analysis followed the procedure of oven drying of the sample at 105 °C for 1 hour to remove moisture. 10 g of sample weighed + 1 g of wax (Hoechst Wax C micropowder) were transfer into Retsch mini mill to homogenize. The homogenized powder was then transfer into the Herzog press with a sample ring and press into a pellet. Excess powder around the pellet was cleaned, and caution taken to avoid touching the surface of the pellet, just to avoid contamination prior to analysis. The analysis commenced using the Quant'X XRF analyzer linked to a PC with Launch Acquisition Manager (LAM) application. In the LAM, sample identification details (IDs) were logged and the required method file chosen for analysis. The method file used was the New Clay calibration for clay, shale, or other siliceous material. The in-house protocol of CBI Analysis 12-12-19-12-03-2022 for cement, clinker, gypsum and limestone was adopted. The experiment

Table 1
Recipe and fineness analysis based on test dates.

		Recipe				Fineness	
Test Date	Samples	Clinker (%)	Black shale (%)	Limestone (%)	Gypsum (%)	Blaine (cm^2/g)	Residue (%)
30/03/2022	Sample 1	73.00	5.00	18.00	4.00	4762.00	11.50
31/03/2022	Sample 2	73.00	10.00	13.00	4.00	4527.00	12.00
01/04/2022	Sample 3	73.00	15.00	8.00	4.00	4581.00	12.50
02/04/2022	Sample 4	73.00	23.00	0.00	4.00	4541.00	10.80
03/04/2022	Sample 5	73.00	0.00	23.00	4.00	4759.00	10.80
04/04/2022	Sample 6	100.00	0.00	0.00	0.00	3543.00	12.40

commenced, and lasted for 10 min in each analysis to complete. The results from the analysis displayed afterwards, details were subsequently copied, and saved in an excel format.

3.1. Cement preparation

The preparation of laboratory cement samples involved grinding various proportions of raw materials using a laboratory mill (Fig. 4a). These raw materials included clinker, limestone, gypsum, and black shale obtained from Apersua (Fig. 4b). After grinding, the materials were sieved to achieve a desired fine particle size distribution. Table 1 details the specific proportions of each raw material used, and the targeted fineness level achieved through grinding. Fineness is a critical factor in cement processing, as it significantly impacts the reactivity of the final product. In this study, the laboratory cement was ground to a Blaine fineness of 4500–4900 cm^2/g, with a sieve retention of 10–13 %.

Following the preparation of the cement samples, a series of laboratory tests were conducted to assess their quality. These tests adhered to the [25] standard, a comprehensive guideline for cement testing methods. The [25] standard encompasses various parts, each focusing on a specific aspect of cement quality such as strength determination [25], cement chemistry analysis [25], and setting times and soundness determination [25]. The cement chemistry analysis covers measuring the Loss-On-Ignition (LOI), insoluble residue and the amount of sulphate (SO_3) present. The setting time include an Initial Setting Time (IST) and a Final Setting Time (FST). The IST marks the point when the mixture begins to stiffen, while the FST indicates when it has achieved substantial rigidity. The soundness test was achieved using the Le Chatelier apparatus specifically designed to measure the expansion of cement paste. This test works by placing a precisely measured cement paste sample (typically 300 g $\pm$ 1 g) inside the mold. The expansion of the cement paste due to the hydration process pushes against the mold walls, and the gauge needles record this expansion.

4. Result

The research findings were carried out based on two forms of datasets: geological data and cement testing data. The geological data category includes information obtained through field observations, thin section, petrographic analysis, and instrumental analyses. Petrographic microscopy helped identify minerals, while X-ray diffraction (XRD) and X-ray fluorescence (XRF) provided data on the elemental composition of the geological materials. The cement testing data category presents the results of various tests performed on the cement samples, including compressive strength and activity index, setting time, water consistency and chemical composition (sulphate content, loss on ignition, and the presence of insoluble residue). This categorization facilitates further discussion on the connection between the geological origin of the materials and their suitability for use in engineering applications, particularly as

Fig. 2. (a) Field photos showing a cliff face of a darker shales outcrop. (b) Broken black shales showing depth extension as a result of excavation (c) Shale show typical laminated feature.

supplements in the cement manufacturing process.

4.1. Geological examination and assessment of rock samples

The rock samples collected from the field (Fig. 2a–c) were classified based on their textural characteristics and mineral composition. The rock is thinly layered with a rhythmic pattern. It appears dark and fine-grained, with a rich composition of clay minerals, primarily interwoven with microscopic quartz (Fig. 3). Minor opaque minerals were also present (Fig. 3b). Some faint, wavy features (Fig. 3c) might be remnants of dewatering or lithification processes. Additionally, Fig. 3d shows thicker laminae dominated by micron size quartz grains. Based on the visual observations and X-ray diffraction analysis (Table 2), the samples were identified as shale with some siliceous portions, indicating the presence of wacke (a type of rock rich in fine quartz grains and clay minerals). The X-ray diffraction data revealed quartz (35–56 %) and various clay minerals as its main components. These clay minerals include muscovite (22–38 %), kaolinite (7–17 %), illite/illite-smectite (5–14 %), and minor chlorite (<2 %). Fig. 4a visually confirms quartz, muscovite, and kaolinite as the most prominent phases. Other minerals were also identified in trace amounts (less than 1 % by modal abundance) through X-ray diffraction (Table 2 and Fig. 4b). These include microcline (a type of feldspar), calcite, dolomite, anatase, pyrite, montmorillonite, diaspore, and pyrophyllite. The X-ray fluorescence data (Table 3) confirmed the presence of major elements like silicon dioxide (SiO_2), aluminum oxide (Al_2O_3), iron oxide (Fe_2O_3), and potassium oxide (K_2O). These elements correspond to the major mineral phases identified by X-ray diffraction, such as quartz, kaolinite, muscovite, chlorite, and microcline. All other elements detected were present in trace amounts (less than 1 wt.%) (see Table 4).

4.2. Cement preparation result (chemical and physical result)

4.2.1. Compressive strength

The cement grades, designated as 32.5 and 42.5, indicate the minimum compressive strength a cement should achieve after 28 days of curing, as specified by standards like [25] EN 196–2:2016. In this research work, the produced cement falls under the 42.5 grade with a CEM II classification according to the [25] EN 196–2:2016 standards (CEM II refers to a specific type of cement with SCMs). The compressive strength of the cement samples was measured at various ages (Fig. 5a and b). The data shows that compressive strength generally increases with age for all samples (Fig. 5a). However, the rate of strength gained varied between samples (Fig. 5b). Sample 6 exhibited the lowest early strength but achieved the highest late strength (Fig. 5a). Sample 2 despite having the highest early strength did not necessarily maintain the lead in later stages (Fig. 5a). Interestingly, samples containing SCMs displayed similar strength

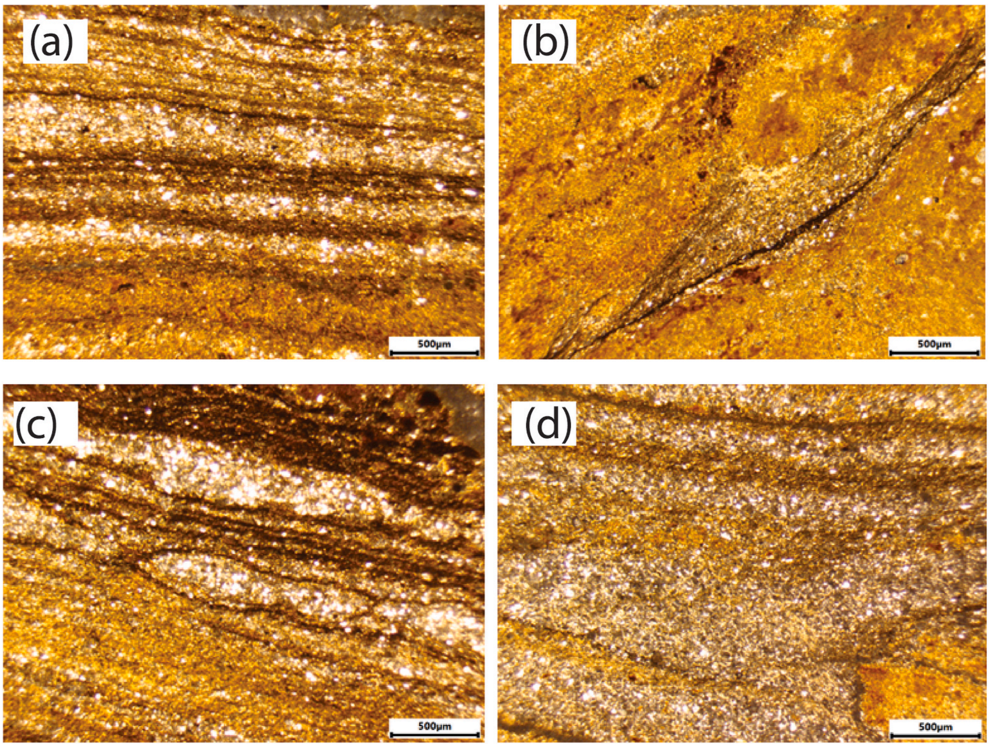

Fig. 3. Photomicrographs of the Apersua samples showing a general presence of sericite (flakes of muscovite), chlorite and micron-sized quartz, and (a) rhythmic laminars of clay-rich and variable micron-sized quartz. (b) The central part shows micron-sized opaques phases along planes (c) poorly developed anastomosing or wavy feature (d) Micron quartz-rich portion with weak laminar at midway, and thick laminar at the upper part.

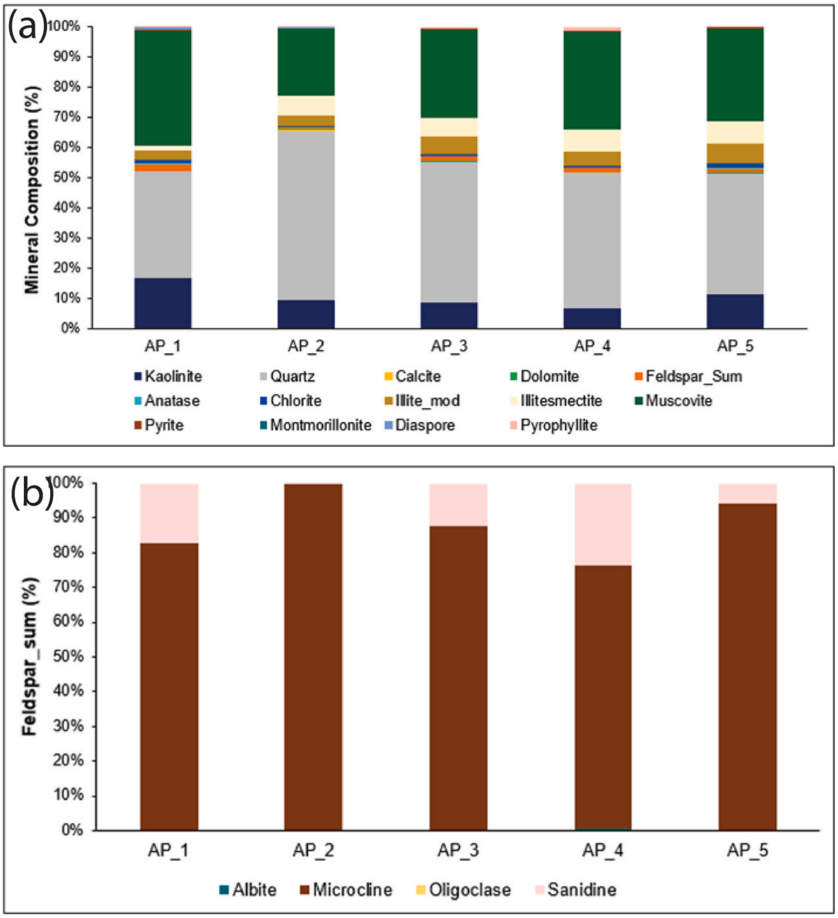

Fig. 4. Graphical display of XRD mineralogical composition of Apersua shaly rocks (a) All the minerals obtained both as dominate-moderate to trace (b) Feldspars are mostly microcline and sanidine dominated.

Table 2
XRD data indicating the mineralogical composition of shale samples from Apersua, Eastern Region- Ghana.

Minerals	AP 1	AP 2	AP 3	AP 4	AP 5
Kaolinite	16.61	9.35	8.55	6.85	11.4
Quartz	35.37	56.42	46.48	44.93	40.06
Calcite	0.06	0.09	0.13	0.02	0.04
Dolomite	0.25	0.35	0.35	0.11	0.19
Albite	0.00	0.00	0.00	0.01	0.00
Chlorite	1.37	0.52	0.63	0.56	1.41
Illite_mod	3.05	3.45	5.59	4.89	6.66
Illitesmectite	1.60	6.50	6.31	7.25	7.19
Muscovite	38.17	22.29	29.36	32.46	30.64
Pyrite	0.13	0.04	0.12	0.11	0.41
Montmorillonite	0.00	0.00	0.06	0.02	0.01
Diaspore	0.95	0.13	0.1	0.12	0.08
Pyrophyllite	0.05	0.31	0.52	1.29	0.19
Anatase	0.34	0.00	0.34	0.00	0.35
Microcline	1.69	0.55	1.28	1.06	1.30
Sanidine	0.35	0.00	0.18	0.33	0.08
Sum	99.99	100.00	100.00	100.01	100.01

development across all the testing stages, with a relatively consistent rate of increase (Fig. 5a). Sample 4, which included only black shale as an additive, showed slightly lower strength compared to the other samples with SCMs (Fig. 5b). It is important to note that all the cement samples satisfied the required strength specifications, demonstrating their suitability for construction applications.

Table 3
Major oxide geochemistry of Apersua samples, Eastern Region- Ghana.

	AP1	AP2	AP3	AP4	AP5
SiO_2	60.07	75.15	72.31	71.60	67.13
Al_2O_3	17.05	16.78	18.39	19.06	18.81
Fe_2O_3	17.33	2.94	3.44	3.21	7.99
CaO	0.32	0.09	0.04	0.11	0.05
MgO	0.85	0.73	0.76	0.77	0.80
Na_2O	0.00	0.19	0.19	0.19	0.22
K_2O	3.09	3.16	3.82	3.94	3.80
TiO_2	0.74	0.76	0.82	0.89	0.88
MnO	0.32	0.01	0.02	0.01	0.11
P_2O_5	0.05	0.05	0.05	0.05	0.04
BaO	0.07	0.08	0.09	0.10	0.09
S	0.08	0.04	0.04	0.05	0.04
Cr_2O_3	0.01	0.01	0.01	0.01	0.01
ZnO	0.01	0.01	0.01	0.01	0.01
SrO	0.01	0.01	0.01	0.01	0.01
Sum	100.00	100.00	100.00	100.00	100.00

Table 4
Compressive strength and activity index information.

Sample ID	Compressive Strength (MPa)					Activity Index (%)		
	1 Day	2 days	7 Days	28 Days	60 Days	7 Days	28 Days	60 Days
Sample1	13.40	25.20	39.70	47.40	51.70	114.00	97.00	96.00
Sample2	13.70	22.10	37.30	46.40	51.50	107.00	95.00	96.00
Sample3	12.30	24.60	38.60	46.80	51.20	111.00	95.00	96.00
Sample4	11.50	20.90	34.50	43.40	47.00	99.00	88.00	88.00
Sample5	13.20	23.50	37.40	48.30	51.40	107.00	98.00	96.00
Sample6	7.40	18.00	34.90	49.10	53.60	100.00	100.00	100.00

4.2.2. Setting time and workability

Setting time is a crucial property for cement, indicating the timeframe during which the cement remains workable before hardening. Several factors, including the addition of SCMs, can influence the setting rate. Another important factor is water consistency, which refers to the amount of water required to make the cement paste workable. However, an excessive water demand for workability can compromise the final compressive strength of the cement. The results in Fig. 6a and b illustrate the relationship between setting time and the composition of the cement samples. Fig. 6a shows a general trend of increasing initial setting time for most samples. This allows for more time to work with the cement before it hardens. However, Sample 6 exhibits a decrease in initial setting time, indicating faster hardening which could be problematic in construction settings. A similar trend is observed for final setting time, with most samples showing an increase. Sample 6 again deviates from this trend, exhibiting a significant rise in final setting time. Fig. 6b presents the data in a bar chart format, allowing for a clearer comparison between samples. Samples 1, 2, and 3 have very similar initial and final setting times, suggesting consistent behaviour. Sample 4, containing only black shale as an additive, has a lower initial setting time compared to Sample 5. This means the cement with black shale starts to harden slightly faster initially. Sample 5, containing only limestone, has a higher final setting time, approaching that of Sample 6.

The most important takeaway from these results is the impact of SCMs on setting time. Sample 6, lacking SCMs, displays the lowest initial setting time and a very high final setting time. This highlights the role of SCMs in regulating the setting behaviour of cement. Without SCMs, the cement may harden too quickly (low initial setting time) and take too long to gain full strength (high final setting time), leading to workability issues during construction.

4.2.3. Standard consistency

Water consistency is a key parameter that reflects the amount of water needed to create a workable cement paste. Ideally, a lower water content is preferable. By analyzing the data presented in Fig. 7a and b, variations in water consistency across the cement samples was observed. Sample 3 exhibits the lowest water consistency, indicating it requires the least amount of water for a workable mix. This is favorable as it can contribute to achieving higher final strength in the cement. Conversely, Sample 6 shows the highest water consistency, signifying an excessive water requirement. Sample 1 also demonstrates a relatively high-water content, similar to Sample 6. Following this trend, the ranking for water consistency, from most desirable to least desirable, would be: Sample 3, Sample 2, Sample 5, and then Sample 4.

4.2.4. Chemical tests

The sulphate content of cement, indicated by the amount of sulphur trioxide (SO_3) present, plays a role in regulating setting time. Ideally, a content around 2.5 % is considered optimal for a balanced setting behaviour. As shown in Table 6 and Fig. 8a, all samples

Fig. 5. (a) Compressive strength increases in days (b) Compressive strength showing increasing trend in days.

except Sample 6 fall within a narrow range of 2.29 %–2.43 % SO_3 content, meeting this requirement. Generally, a higher SO_3 content leads to a longer setting time, while a lower content results in faster setting.

Loss on Ignition (LOI) and Insoluble Residue (IR), as indicated in Table 6, are both indicators of the cementitious material content in cement. Fig. 8b and c shows the LOI values for all samples. Sample 5 exhibits the highest LOI value, whereas Sample 6 has the lowest. In Sample 6, the high clinker content (100 % according to Table 1), a highly cementitious material, likely contributes to the lower LOI. In contrast, Sample 5 contains limestone and gypsum, which are less cementitious, and black shale, an uncementitious material. However, despite the higher LOI, Sample 5's value remains within the acceptable range, suggesting it can be a suitable substitute. The values for insoluble residue in all samples (refer to Table 6) also fall within the acceptable limits.

5. Discussion

5.1. Apersua shale as suitable cementitious material

This research investigated the potential of argillaceous rocks from the Apersua area as supplementary cementitious materials (SCMs) in cement manufacturing. SCMs are materials that can be added to cement to improve its properties, such as workability, strength, and durability. The study involved laboratory experiments where Apersua rock samples were incorporated in various proportions into cement recipes (Table 1). Six different cement samples were prepared using combinations of clinker (the main binding component in cement), black shale (from Apersua), limestone, and gypsum (Table 1). These prepared samples then underwent a series of physical and chemical tests to determine if they meet the standards for SCM cements (e.g., pozzolan, slag, fly ash) as defined by international specifications like [1]. A key aspect of this research was the focus on the recipe design before property testing. This approach allowed for the identification of optimal combinations for creating effective SCMs. Additionally, the study incorporated field observations, petrographic analysis of mineral composition, and elemental analysis of major oxides (Table 2). This comprehensive approach aligns with the recommended standards outlined in Ref. [26] for evaluating alternative SCMs [27].

Beyond the standard physical and chemical tests on the prepared cements (Samples 1–6 in Table 1), the research employed a diverse testing timeline (day 1, 2, 3, 7, 28, and 60 days). This extended testing period allowed for a thorough assessment of the

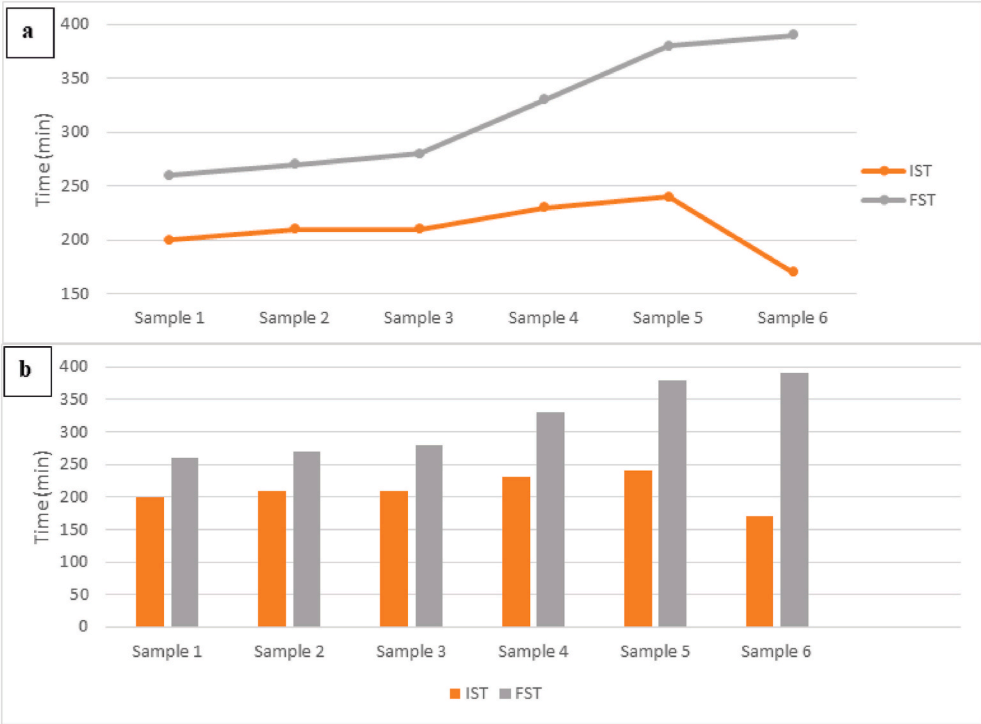

Fig. 6. (a) Trendline showing the highs and lows of the Initial (IST) and Final Setting Times (FST) (b) Comparison of Initial and Final Setting Times.

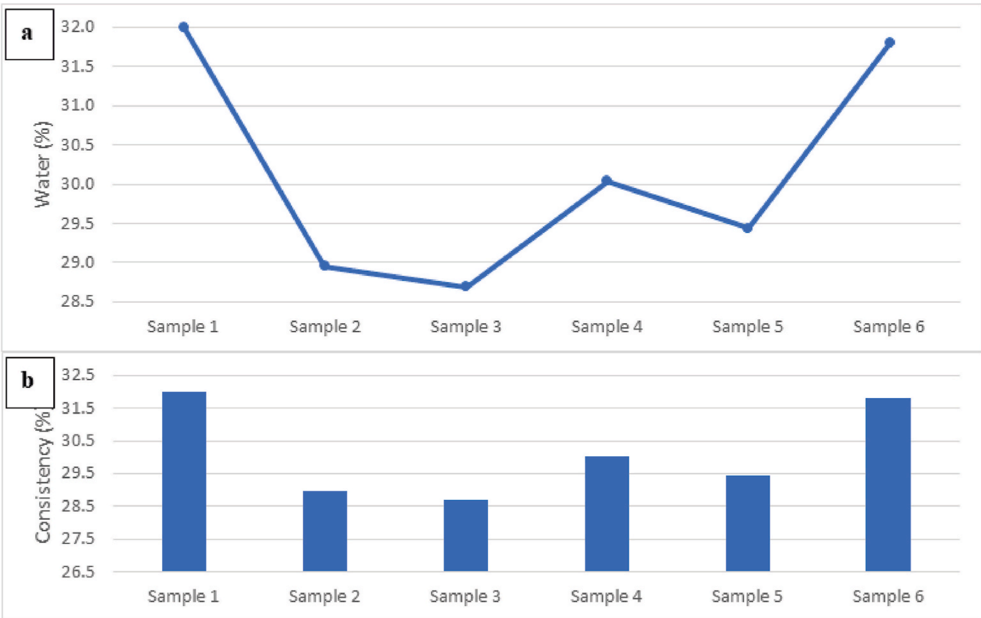

Fig. 7. (a) Trendline showing the Water Consistency in percentages. (b) Comparison of Consistency values.

material's suitability for its intended purpose, particularly focusing on its strength development over time. The fineness of the cement powder, measured by Blaine fineness and residue on a sieve, is an important property that influences its reactivity and strength development. This study investigated the impact of incorporating Apersua shaly materials (samples 1–4) alongside varying limestone content (0–18 %) on the fineness of the final cement product (Table 1). All these samples, containing 4 % gypsum, exhibited fineness values within the acceptable range. Interestingly, Sample 5, which lacked Apersua shale but included limestone and gypsum, also

Table 5
Setting time based on water consistency in samples.

Sample ID	Water Consistency (%)	Initial Setting Time IST (min)	Final Setting Time FST (min)
Sample 1	32.00	200.00	260.00
Sample 2	29.00	210.00	270.00
Sample 3	28.70	210.00	280.00
Sample 4	30.00	230.00	330.00
Sample 5	29.40	240.00	380.00
Sample 6	31.80	170.00	390.00

Table 6
Details of chemical test of SO_3, LOI and IR.

Sample ID	Sulphate (SO_3)	Loss on Ignition (LOI)	Insoluble Residue (IR)
Sample 1	2.43	6.77	10.45
Sample 2	2.4	6.03	13.96
Sample 3	2.38	5.09	13.97
Sample 4	2.29	4.06	21.02
Sample 5	2.41	7.89	12.52
Sample 6	0.83	1.31	0.06

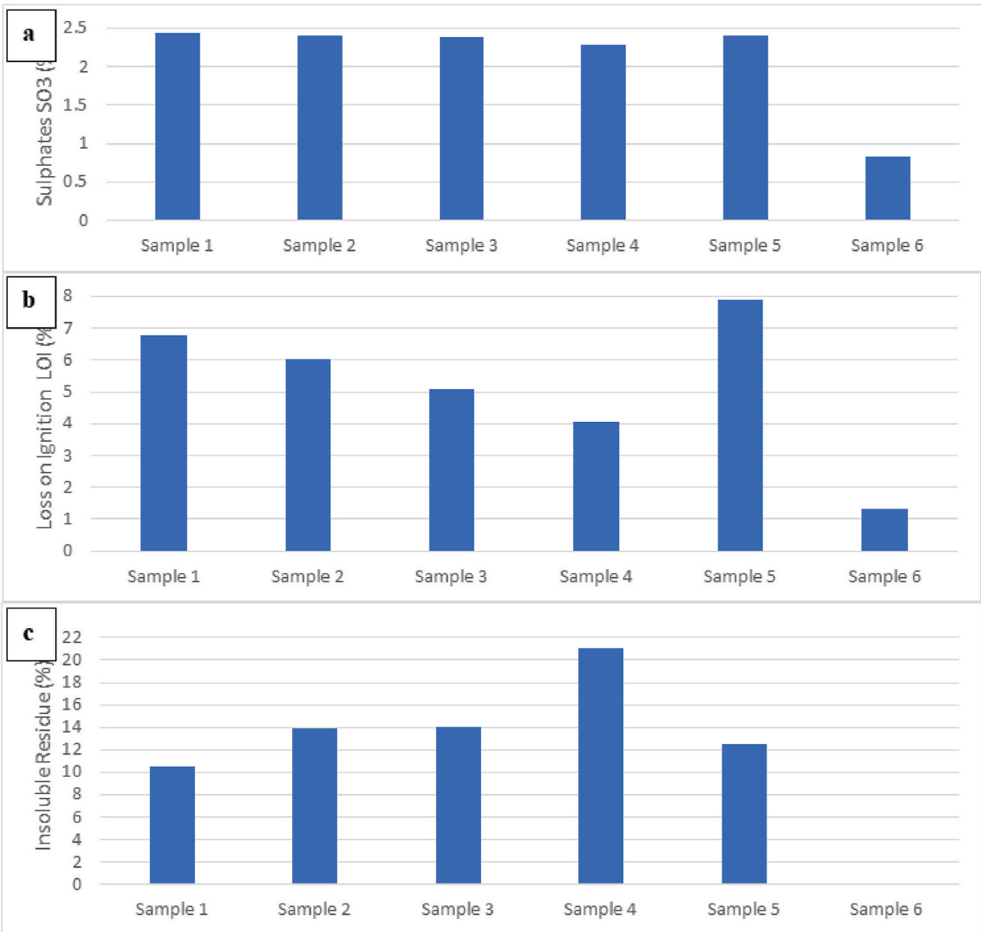

Fig. 8. (a) Shows a comparison of the Sulphates (SO_3) (b) Shows a comparison of the Loss on Ignition (LOI) (c) Shows a comparison of the Insoluble Residues (IR).

displayed similar fineness results. This aligns with expectations as limestone and gypsum are well-established SCMs known for their grinding properties [28]. However, the comparable fineness results between samples with and without Apersua shale suggest that the Apersua shaly material itself can also contribute to achieving the desired fineness, potentially acting as a grinding aid during the cement production process. This observation supports the potential usability of Apersua shale as a viable cementitious material.

The setting time data in Table 5 and Fig. 6a & b further strengthens the case for Apersua shales as potential SCMs. Sample 6, consisting entirely of clinker (no SCMs), exhibits a lower initial setting time (IST) (Fig. 6a) and a significantly higher final setting time (FST) (Fig. 6b) compared to all samples containing combinations of limestone, Apersua shale, and gypsum. Samples 1 to 4, containing Apersua shale with varying limestone content, all have IST values within a narrow range of 200–230 min. This range is even closer to the IST of Sample 5 (240 min), which only includes limestone and gypsum. This suggests that the presence of limestone, a known setting time modifier, might be influencing the IST in these samples. Interestingly, the higher FST observed for samples 4, 5, and 6 (compared to samples 1, 2, and 3) suggests that the absence of Apersua shale and limestone (or any SCMs) in cement preparation, while maintaining consistent water content (28–32 %, Table 5), can potentially lead to a significantly extended FST (over 60 min). Cements with a very low IST and very high FST can be problematic due to workability issues. Despite the observed variations in setting time, all samples displayed a progressive increase in compressive strength from day 1 to day 60. However, it's important to remember that compressive strength alone is not the sole determining factor for a suitable SCM. Other factors, as outlined by Refs. [27,29,30], also play a critical role in the evaluation process. These factors include mineralogical composition, chemical tests (sulphate content, heavy metals, alkalis, etc.), and fineness.

The suitability of Apersua shales as SCMs is strongly supported by the combined findings from multiple analyses. The petrographic observations (Figs. 2 and 3) provided insights into the rock textures and mineral compositions of the Apersua samples. The

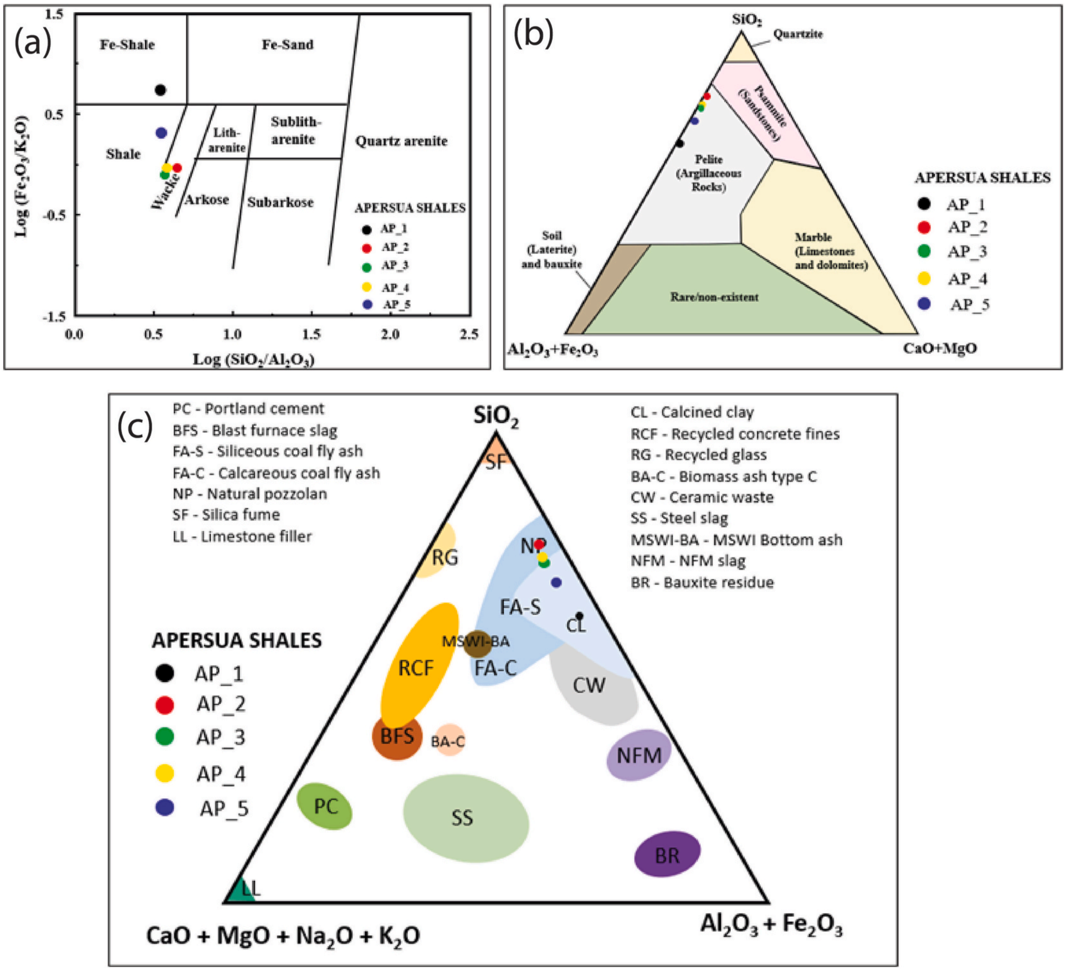

Fig. 9. Apersua rock samples compared to various geochemical plots and documented supplementary cementitious materials (SCMs) (a) Apersua samples classified as shales and wackes using log (SiO_2/Al_2O_3) -log (Fe_2O_3/K_2O) diagram after Ref. [33]. (b) Apersua shales as mainly argillaceous materials based on geochemical plot by Ref. [34]. (c) Apersua samples compared to other SCMs (similar to natural pozzolan, calcined clay and silicious coal fly ash) in a ternary diagram (earth)alkalis–silica–alumina/iron oxide (in wt%) (Diagram adopted from Ref. [6]. NFM stands for "non-ferrous metallurgical", MSWI for "municipal solid waste incineration".

mineralogical composition (Table 2, Fig. 4a & b) from the X-ray diffraction analysis revealed the specific minerals present in the Apersua shales. The Major oxide elemental composition (Table 3) identified the key chemical elements that make up the Apersua shales. Laboratory cement analyses (Table 6) measured properties relevant to cement production, including sulphate content, insoluble residue, and loss on ignition. Collectively, this data aligns with established evaluation methods for Ordinary Portland Cement (OPC) and SCMs, as outlined by Refs. [28,31,32], and [26] standards. By considering these various aspects, the research effectively demonstrates the potential of Apersua shales as a viable SCM option.

5.2. Mineralogy and geochemical significance of the Apersua rocks to other SCMs

The geochemical analysis of Apersua shales (Fig. 9a and b & Table 2) provides valuable insights into their suitability as SCMs. Fig. 9a confirms the presence of shale and wacke characteristics in the Apersua rocks, indicated by an increase in micron-sized quartz content. Fig. 9b classifies the Apersua samples as primarily pelites, with a dominant clay mineral or phyllosilicate composition (argillaceous). This is further supported by the X-ray diffraction data in Table 2, which reveals a significant presence of quartz (35–56 %) and various clay minerals like muscovite (22–38 %), kaolinite (7–17 %), illite/illite-smectite (5–14 %), and minor chlorite ($<$2 %). The limited presence of metallic or sulfide phases in the Apersua shales (Tables 2 and 3) is a positive attribute for SCMs. Research by Refs. [27,29,30] highlights the detrimental effects of heavy metals and sulphate attack in cement and concrete.

The X-ray fluorescence data (Table 3) confirms the dominance of elements like silicon dioxide (SiO_2), aluminum oxide (Al_2O_3), iron oxide (Fe_2O_3), and potassium oxide (K_2O). These elements correspond to the major minerals identified by XRD, such as quartz, kaolinite, muscovite, chlorite, and microcline. The combined mineralogical and geochemical properties suggest that Apersua rocks are promising candidates for SCMs. Studies by Refs. [5,9,10] have shown that favorable geochemical and mineralogical attributes in rocks can enhance the performance of low-clinker cements and concrete. Similarly, other experimental works have pointed out geochemical positive effect of enhancing compressive strengthen besides SCMs as reliable substitutes [11,12,35]. To further strengthen the case for Apersua shales as potential SCMs, Fig. 9c compares their geochemical composition to globally recognized SCMs using a ternary diagram based on SiO_2, $CaO + MgO + Na_2O + K_2O$, and $Al_2O_3+Fe_2O_3$. The diagram reveals that the Apersua samples align closely with natural pozzolan, calcined clay, and siliceous coal fly ash. It's important to note that while siliceous coal fly ash appears as a potential match, the geological context of the Voltaian Supergroup in Ghana (where coal fly ash is not typically reported) may necessitate further investigation into its provenance. Nevertheless, based on the ternary plot and major oxide classification, the geochemical features of the Apersua samples suggest strong potential as SCMs, particularly as chemical admixtures to improve the performance of low-clinker cements and concrete. Table 1 further supports this application by demonstrating the successful use of varying Apersua shale portions (5 %–23 %) in the cement preparation process.

6. Conclusion and recommendation

By integrating various analyses, including field observations, petrographic studies, X-ray diffraction (XRD) for mineralogy, X-ray fluorescence (XRF) for elemental composition, and laboratory cement tests, this research reached the following conclusions.

- The Apersua samples, primarily composed of shales with some wacke (containing increased micron-sized quartz), exhibit cementitious properties due to their mineral phases. This suggests their potential as supplementary cementitious materials (SCMs) with various functional benefits in cement.
- The compressive strength of cement samples prepared with and without Apersua shales showed comparable results. All samples exhibited an appreciable growth rate and met the required cement specifications according to EN 196. Notably, the sample containing only black shale (without limestone) displayed slightly lower strength but still surpassed the EN 196 standards.
- Based on the analysis of compressive strength, chemical tests, setting time, and soundness, the Apersua shales demonstrate promising potential for commercial use as SCMs.
- The incorporation of black shale in cement production influences the final colour. As a result, the cement takes on a darker shade compared to the standard grey or brownish colour. While colour does not directly impact strength or durability, it can enhance the visual appeal and marketability of the cement, potentially increasing its market sustainability.
- The successful application of Apersua rocks in cement production adds economic value to the material. Mining this resource can potentially create economic opportunities for residents in the Apersua area.

CRediT authorship contribution statement

Samuel Nunoo: Writing – review & editing, Writing – original draft, Data curation, Conceptualization. **Theresa A. Owusu-Sasu:** Writing – original draft, Methodology, Investigation, Conceptualization. **Prince O. Amponsah:** Writing – review & editing, Writing – original draft, Methodology, Data curation, Conceptualization. **Francis Achampong:** Writing – original draft, Visualization. **Mahamuda Abu:** Writing – review & editing, Writing – original draft, Conceptualization. **Eric D. Forson:** Writing – review & editing, Writing – original draft, Conceptualization. **Edward K. Ackom:** Writing – original draft, Methodology. **Remi Touvet:** Writing – review & editing, Writing – original draft, Conceptualization. **Peter Dickson:** Writing – review & editing, Writing – original draft, Resources, Project administration. **Larry P. Chegbeleh:** Writing – review & editing, Investigation, Conceptualization.

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.

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