Iraqi National Journal of Earth Science

www.earth.mosuljournals.com

Experimental Investigations of Some Clays Industrial Wastes as Recyclable Materials for the Production of Blended Cement

Hatem M. El-Desoky [1], **Mohamed A. Heikal** [2], **Gehad M. Saleh** [3], **Ramadan E. El-Shafey** [4*], **Hamada M. El-Awny** [5]

[1,2,4,5] *Department of Geology, Faculty of Science, Al-Azhar University, Egypt.*

[3] *Nuclear Materials Authority (NMA), Egypt.*

Article information

Received: 15- Jul -2023

Revised: 07- Aug -2023

Accepted:18- Sep -2023

Available online: 01- Jul - 2024

Keywords:
Blended cement
Pozzolana
calcium aluminate silicate hydrates (CASH)
silicates solid waste
industrial waste material

Correspondence:
Name: Ramadan Elsayed Elshafey
Email:
Eng.ramadan.elshafey@gmail.com

ABSTRACT

This study deals with a comparative experimental investigation of industrial waste clays as recyclable materials in blended cement production. Even though waste of fired clay bricks (WFCBs), ground or broken bricks, waste of ceramic tiles (WCTs), and waste of vitrified clay pipes (WVCPs) are silicate solid waste, their recycling management has the best environmental, social, and economic aspects. The implementation of these wastes as recyclable materials in wall materials, mortar, and concrete are used as raw materials or cement additives as pozzolanic materials for rapid urbanization and improvement of construction and high pollution rates in developing countries such as Egypt. A large amount of these wastes has been produced by factories for producing clay bricks, ceramic tiles, and vitrified clay pipes, as well as construction operations, building improvement, and the demolition of old buildings. The mortar's microscopic structures are observed by scanning an electronic microscope (SEM), while hydrous minerals are studied using X-ray diffraction (XRD) as well as differential thermal analysis (DTA). These wastes, as artificial pozzolanic materials, raise the setting time of cement products. The average strength of compressive and flexural accelerates at an early age slower than later age. The study aims to reduce construction solid waste and conserve raw material resources. These wastes are widespread in the Egyptian provinces, and there is very little available information on their chemical composition and mineral components.

DOI: 10.33899/earth.2023.141800.1111,

التجارب المعملية لبعض مخلفات تصنيع الطين لإعادة استخدامها في إنتاج الأسمنت المخلوط

حاتم محمد الدسوقى[1] ، محمد أحمد هيكل[2] ، جهاد محمد صالح[3] ، رمضان السيد الشافعي[4]* ، حمادة مجلي العونى[5]

[5،4،2،1] *قسم علوم الأرض، كلية العلوم ، جامعة الأزهر ، مصر.*

[3] *هيئة المواد النووية ، مصر.*

معلومات الارشفة

تاريخ الاستلام: 15- يوليو -2023

تاريخ المراجعة: 07- أغسطس -2023

تاريخ القبـول: 18- سبتمبر -2023

تاريخ النشر الالكتروني: 01- يوليو -2024

الكلمات المفتاحية:

الأسمنت المخلوط

البوزولانا

ألومينوسيليكات الكالسيوم المميهة

المخلفات الصلبة السيليكاتية

مواد المخلفات الصناعية

المراسلة:

الاسم: رمضان السيد الشافعى

Email: Eng.ramadan.elshafey@gmail.com

الملخص

تتناول هذه الدراسة تجارب معملية على مخلفات التصنيع الطينى كمواد قابلة لإعادة التدوير فى إنتاج الأسمنت المخلوط، وهذه المخلفات عبارة عن مخلفات سيليكاتية صلبة وإدارتها لإعادة استخدامها فى إنتاج الأسمنت المخلوط لها مميزات بيئية وإقتصادية وإجتماعية عالية نظرا لعمليات التوسع والتطوير والتحسين العمرانى والبنية التحتية للدول النامية ومنها مصر. ولهذا السبب تتوافر هذه المخلفات بكميات كبيرة من عمليات التصنيع والهدم والتطوير وتحتاج إلى دراسات كافية لمعرفة تركيبها الكيميائى والمعدنى. تم التأكيد بعد الفحص للمكونات المعدنية بواسطة المجهر الألكترونى وحيود الأشعة السينية من أن هذه المخلفات لها خاصية بوزولانية وأن إضافة هذه المخلفات تزيد من زمن الشك الأبتدائي والنهائي وقوة تحملها للضغط تزداد مع الوقت. وخلصت الدراسة إلى أن إستخدام هذه المخلفات لها تأثير إيجابي على البيئة والحفاظ على الموارد الخام الطبيعية الداخلة فى صناعة الأسمنت وإدارة هذه المخلفات لما لها من تأثير إيجابى اقتصاديا على الدول النامية فلا بد من وجود سياسات وإستراتيجيات تلبى وتخدم إعادة إستخدام هذه المخلفات.

DOI: 10.33899/earth.2023.141800.1111, ©Authors, 2024, College of Science, University of Mosul.

Introduction

In the late twentieth century, there was an increasing awareness of the overall impacts of cement manufacturing on the atmosphere. The impact of CO_2 has been considered one of the major factors affecting climate change. The CO_2 is emitted as a result of cement production with the amount reaching about 0.9 tonne per tonne of clinker production. Concrete production has an impact on climate as it accounts for 5-7% of total anthropogenic carbon dioxide emissions (Meyer, 2009). It is commonly known that the cement industry needs high energy consumption and emits a lot of greenhouse gases (Reddy *et al*., 2003). The energy consumption and carbon footprint of the building materials are effectively decreased by the partial substitution of cementing materials for non-conventional binders. Ceramic wastes are used as partial replacement in blended cement and affect the physic-mechanical properties of produced concrete; it is found that the ideal partial replacement ratio by these wastes reaches up to 25% to produce lightweight foamed concrete (Siong *et al*., 2022). The characteristics of blended cement containing up to 50% pulverized fired clay brick wastes are the superior properties values and it is concluded that the prepared mortar is attained at a level of 20% replacement by the waste after treatment time at 28 days (Oluwarotimi *et al*., 2019). The influence of pozzolanic activity on the properties of blended cement mortar at partial replacement of clay brick powder waste that was collected from a demolition place surrounding Nanjing, the pozzolanic activity was enhanced decreased with particle size clay brick powder (Yasong *et al*., 2020). The investigation of some Egyptian clay materials in vitrified clay pipe production reveals that these clay materials are appropriate for clay pipe production (El-Desoky *et al*., 2019). Based on the properties of produced fired clay bricks, the Egyptian Paleozoic raw building materials have been investigated with different mixes. The better mix has been assigned with 10% sand at a burning temperature equal to or over 800°C (Adel *et al*., 2022). Some Egyptian raw materials comprise quartz, kaolin, feldspar, and bentonite for the production of ceramic tiles, sintered between 1160 to 1260°C, and the main fired minerals are mullite, quartz, and albite (Mohamed *et al*., 2021). However, pozzolans are of both natural and artificial origin. The natural pozzolans are of volcanic origin such as volcanic ash, pumice, zeolite, and tuffs. Artificial pozzolans are waste products formed from industry or heat treatments for clays such as metakaolin (MK), silica fume (SF), granulated blast furnace slag (GBFS), fly ash (FA), calcined clays or shales, and rice husk ash (RHA) as well as wastes of clays manufacturing (Hewlett, 1998, Soroka, 1979, Ramachandran *et al*., 1999 and Singh *et al*., 2001). The Romans were the first users of lime incorporating natural materials to produce highly durable hydraulic binders and are the oldest construction materials that were used before cement invention in the 1700s (Malinowski *et al*., 1991; Spence *et al*., 1974). Pozzolanic reaction calcium hydroxide generated by calcium silicate hydrate and calcium aluminosilicates hydrate with desired durability and binding characteristics, pozzolans enhance the properties of blended types of cement, and different clinker substitution levels can be published stand on the type and surface area of pozzolans and properties of the Ordinary Portland Cement (OPC) (Hewlett *et al*., 1998 and Ramachandran *et al*., 1999). It is widely believed that the calcined artificial pozzolans, such as calcined clays, at an ideal temperature of 800-850°C would produce the most pozzolanic reactivity (Wild *et al*., 1996). The fire behaviors of clays are controlled by their chemical and mineralogical constituents (Murat, 1983). A large amount of waste-fired clay bricks WFCBs has been generated from the demolition of buildings, and according to statistics, the number of WFCBs generated from the demolition waste and building operations are about 50-70% and 30-50% respectively (Li, 2005). The worldwide annual production of bricks in 2015 was 1500 billion units and the annual demand for bricks is expected to increase continuously by 5-6% (Halblazig –Zig, 2014 and 2019). A lot of researchers have proposed that the use of WFCBs as pozzolanic materials in blended cement improves some properties and minimizes the production cost. Moreover, when cement clinker is partly replaced by WFCBs with different percentages (0-50 %), the strength value of mortar would be raised to 10% cement replacement (Naceri *et al*., 2009, Cheng *et al*. and Tian 2014, Wang, 2012 and Ma, CT., 2009). When the percentage of WFCBs increased above 10%, the compressive strength of mortar had reduced (Wu XM, 2004). When cement clinker is partially replaced by clay brick waste, the strength accelerates slowly at the early stage of hydration, and the setting time and water of consistency are increased (Lin *et al*., 2010; Han *et al*., 2015). When the replacement level of calcined clay brick waste is 20% from cement, it is estimated to reduce CO_2 emissions by about 10% (Toledo *et al*., 2007). Incorporating OPC paste up to 25 % with Homra (ground-fired defective clay bricks) improved the compressive strength when the dose of Homra was 20 wt%. Furthermore, the paste cement mix with Homra is thermally stable between 100ºC and 400°C, and additional C-S-H cement compounds resulting from the pozzolanic reaction reduce the pore system (Heikal, 2000). Loss on ignition for different hardened paste cement is raised with increasing Homra content as well as temperature increase. Also, the apparent porosity is raised while density decreases at temperatures between 400 - 500ºC (Darweesh, 2017). Some researchers have provided that the use of waste ceramic tiles (WCTs) as pozzolanic materials can improve some engineering properties, and reduce the production cost. Incorporating OPC paste with (TCW) up to 35 wt% satisfies the strength activity index (SAI) fixed by fly ash limitations (Maria *et al*., 2016). Ceramic waste can be used as a pozzolanic material to decrease CO2 emission and stabilize hydration heat for up to 28 hours. The WCT addition consumes, partially, the CH by pozzolanic reaction affecting the decreasing of both compressive strength at an early age and the porosity as well as specimen density (Viviana *et al*., 2019). Ground waste ceramic has been applied in blended cement (CEMII) with a substitution ratio of 35%. The use of a 5% replacement level by ground ceramic does not affect the control paste and mortar cement, where the CH is converted to CSH through the pozzolanic reaction of ceramic waste (Sadek, 2018). The addition of clay bricks as a partial substitution for white cement led to reduce the whiteness of cement, and delayed setting time of blended cement and porosity. Moreover, it increases water content, compressive strength, and density as a result of the pozzolanic reactivity of fired clay bricks (Mohamed, 2022). Pozzolanic reactivity and compression strength value are improved more slowly at an early stage due to the substitution of clinker with pozzolana. This is related to the rate of the pozzolanic reaction where it is really slow early (Massazza, 1993). At a later stage, the compressive strength increases due to the hydration precedes more new hydration products such as CSH and CASH causing a rise in the compressive strength value of blended cement pastes (Massazza, 1993 and Commite, 1994). The main objective of this study is to investigate the addition of some industrial wastes as a partial replacement of cement clinker on the properties of blended cement mortars.

Materials methods and techniques

Starting raw materials

The used raw materials are Ordinary Portland Cement Clinker (OPCC) delivered from Al-Arish Cement Company (ArCC); fired clay bricks (WFCBs) wastes collected from Mit Ghamr clay bricks; ceramic tiles (WCTs) wastes collected from Ceramic Cleopatra Group; vitrified clay pipes (WVCPs) wastes collected from Sweillem Clay Pipes Company; and gypsum has been extracted from gypsum quarry in Ras Sudr South Sinai. CEN Standard sand shipped in bags with 1350 ± 5g weight from France was used. Distilled water has been used.

Fig.1.Photographs showing industrial waste at landfill sites: (a) WFCBs beside a clay brick factory. (b) Construction area (c) Demolition area. (d) (WCTs) and (e) (WVCPs).

Methods and techniques

The studied industrial waste materials, ordinary Portland cement clinker, and gypsum were crushed and grounded in a ball mill to pass through a 200-mesh sieve size, then quartered. These are conducted in the Centralized Laboratories of the Housing and Building National Research Center (HBRC) and Nuclear Materials Authority (NMA) in Egypt. The prepared materials are analyzed by X-ray fluorescence (XRF) of an Axios sequential spectrometer manufactured by PANalytical, Netherlands. The crystalline phases of clinker studied industrial waste and selectively treated specimens for determining hydration phases, are examined by the XRD technique of a BRUER, Axs D8 ADVANCE A8, and using Germany Diffractometer at Nuclear Materials Authority (NMA) Laboratories. Clinker phases are estimated according to Bogue's equations (Robert, 1929). Calculation of water consistency and setting times of cement pastes have been measured according to the European Standard (BS EN 196-3). Setting times of cement pastes have been performed using Automatic VI vat Needle Apparatus (Toni SET Classic). Compressive and flexural strengths of the lab-made blended cement mortars are executed in the Laboratories of Sinai Cement Company (SCC) and Laboratories of El-Arish Cement Company (ArCC) according to ASTM (C349-18) and ASTM (C348-21) respectively. Schimaduz DTA-50 (Co-Kyoto, Japan) thermal analyzer device is used to identify the hydration phases of cured blended mortars specimens and carried out in Nuclear Materials Authority (NMA) Laboratories. To describe the morphology and micro-structure of broken parts of hardened treated specimens of different mixes, the scanning electron microscope (SEM) is carried out using Model Quanta 250 FEG (Field Emission Gun), with magnification ×14 up to ×1,000,000, accelerating voltage 30 KV and resolution for Gun.1n)

Mix Composition and Mortar specimens preparation

To investigate the effect of industrial wastes on the properties of OPCC, thirteen mixes namely C.0 (blank mix), (C.1-C.12) are designed for study and sand: cement: water ratio, which is 3: 1: 0.5 (Table. 1). To process the experimental work, the mix ingredients have been ground, then mixed in an electrical mixer for 3 minutes, and water has been added and re-mixed until a homogeneous paste was achieved. Then, the cement mortar is poured into 40×40×160 mm steel prism molds. The molds are carefully vibrated to remove the air bubbles. The fresh mortar is maintained in the molds inside a humidity cabinet at 20°C and relative humidity at least 90% for 24 hours before demolding. The hardened specimens are de-molded and treated in a water tank at room ambient conditions till the testing times of 7 and 28 days. At the end of the curing period, a series of tests are carried out to determine the selected properties of the hardened blended cement mortar specimens in terms of compressive and flexural strength tests. The averages of tests on three repeated specimens are calculated.

Table 1. Compositions and properties of the studied mixes (wt.%) incorporating industrial wastes

Mix No.	OPCC	WFCBs	WCTs	WVCPs
C.0	95	-	-	-
C.1	85	10	-	-
C.2	80	15	-	-
C.3	75	20	-	-
C.4	70	25	-	-
C.5	85	-	10	-
C.6	80	-	15	-
C.7	75	-	20	-
C.8	70	-	25	-
C.9	85	-	-	10
C.10	80	-	-	15
C.11	75	-	-	20

Results and Discussion

Chemical characteristics

The oxide compositions of the OPCC sample (Table .2) reveal that the sample is composed primarily of CaO, SiO_2 as well as Al_2O_3 and Fe_2O_3. The calculated clinker phases in decreasing order of abundance are C_3S, C_2S, C_4AF, and C_3A. All studied industrial wastes show that the major elemental oxides are SiO_2, Al_2O_3 as well as Fe_2O_3. CaO is recorded as a minor amount (about 5%) in WFCB and WCT. The composition of gypsum samples shows that the most common chemical composition of gypsum deposits is SO_3 and CaO. The comparative study between standard eligible criteria (BS 8615-1:2019) for pozzolanic activity and present results (Table .3) reflect that all studied wastes achieved all listed parameters for pozzolanic materials.

Table 2. The chemical composition (wt. %) in terms of oxide content, loss on ignition, clinker phase, and free lime for the studied materials.

Oxides	OPCC	WFCBs	WCTs	WVCPs
SiO_2	21.30	63.64	62.55	59.90
Al_2O_3	5.88	18.17	16.22	26.60
Fe_2O_3	4.23	5.56	7.65	8.08
CaO	66.00	4.92	5.38	0.20
MgO	1.25	1.32	0.88	0.40
SO_3	0.69	1.50	1.40	1.20
K_2O	0.20	1.37	2.45	1.24
Na_2O	0.29	0.90	2.11	0.43
TiO_2	0.03	0.94	0.74	1.74
Cl	0.04	0.07	0.05	0.08
P_2O_5	0.08	0.22	0.32	0.13
LOI	0.20	1.46	0.30	0.20

Ordinary Portland cement clinker (OPCC), waste of fired clay bricks (WFCBs), waste of ceramic tiles (WCTs), waste of vitrified clay pipes (WVCPs), free lime (FL), alite (C_3S), (C_2S) belite, aluminate (C_3A) and ferrite (C_4AF).

Table 3. Comparative results between standard eligible criteria for pozzolanic materials according to (BS 8615-1:2019) and the used industrial wastes.

	BS 8615-1:2019		Wastes used		
Property	Result	Test method	WFCBs	WCTs	WVCPs
Loss on ignition	≤ 7.0%	BS EN 196-2	1.45	0.30	0.20
Chloride content	≤ 0.1%	BS EN 196-2	0.07	0.05	0.08
Sulfate content	≤ 3.0%	BS EN 196-2	1.5	1.40	1.20
Free calcium oxide	≤ 1.5 %	BS EN 451-2	0.2	0.00	0.00
Sum of oxides (SiO_2+Al_2O_3+Fe_2O_3)	≥ 70.0%	BS EN 196-2	87.37	86.42	95.3
Magnesium oxide	≤ 4.0%	BS EN 196-2	1.32	2.45	1.20
Reactive calcium oxide	≤ 10.0%	BS EN 196-2	4.92	5.38	0.40

Waste of fired clay bricks (WFCBs), waste of ceramic tiles (WCTs), and waste of vitrified clay pipes (WVCPs).

Mineralogical compositions

The mineralogical composition of the used materials (OPCC, WFCBs, WCTs, and WVCPs) and selected hardened mortars of different mixes (C.0, C.1, C.3, C.5, C.7, C.9, and C.11) are illustrated in XRD patterns (Figs.2 and 3). The XRD pattern of the OPCC sample matched with its chemical phase's composition. The XRD pattern of the WFCB sample shows that it is composed mainly of quartz (SiO_2) and sanidine ($KAlSi_3O_8$). Mineralogically, the WCTs sample is composed of well-crystalized quartz and vaterite ($CaCO_3$) that may be formed from the hydration of stored cement and found by water vapor and air for prolonged contact (Ewa *et al*., 2003). Vaterite is unstable $CaCO_3$ polymorphs and mostly water soluble and gradually changes to calcite (Per, 2003). Also, a poorly crystallized form of mullite ($Al_2O_3.SiO_2$) phase (highly temperature mineral) is detected. The XRD pattern of the WVCPs sample illustrates that the sample is mainly composed of quartz and cristobalite (SiO_2) and a minor amount of mullite phase. XRD pattern (Fig. 3) revealed that blank mortar is composed mainly of quartz and hydration phases of tobermorite $Ca5Si_6O_{16}(OH)_2.4H_2O$ {calcium silicate hydrate, (CSH)} and {portlandite $Ca(OH)_2$,(CH pozzolanic activity increased (hydration phases) and CH decreased due to its consumption in the CASH formation)}. The results prove that as industrial waste increased, the cement clinker amount decreased pozzolanic activity increased (hydration phases) and CH decreased due to its consumption in the CASH formation.

Thermal properties of the hardened blended cement mortars

DTA/TG patterns are used to identify the essential hydrate products shaped by their mass of loss (CSH, CH, C) for the different prepared cements (Alp *et al.*, 2009 Barbara *et al.*, 2016). The DTA and TGA thermograms patterns (Fig. 4) of selected hardened blended cement mortar specimens (C.0, C.1, C.3, C.5, C.7, C.9, and C11) are treated for 28 days show the existence of the endothermic peaks at 51, 96, 473, 481, 493, 634, 700, 718, 722, and 731°C. The endothermic peaks lower than 200°C are generally caused by the dehydration, (free water), tobermorite phase (CSH gel) as well as calcium aluminosilicate hydrate (CASH). It is companied with loss of mass percentages 2, 2, 2.5, 2.2, 2.7, 2.3, and 2.6 (%) for C.0, C.1, C.3, C.5, C.7, C.9, and C.11 respectively. The endothermic peaks between 470° C to 500° C describe the dehydroxylation of $Ca(OH)_2$ (portlandite). It is associated with loss of mass equal to 1.8, 1.2, 0.8, 1.15, 0.7, 1.1, and 0.9 (%) for C.0, C.1, C.3, C.5, C.7, C.9, and C.11 respectively.

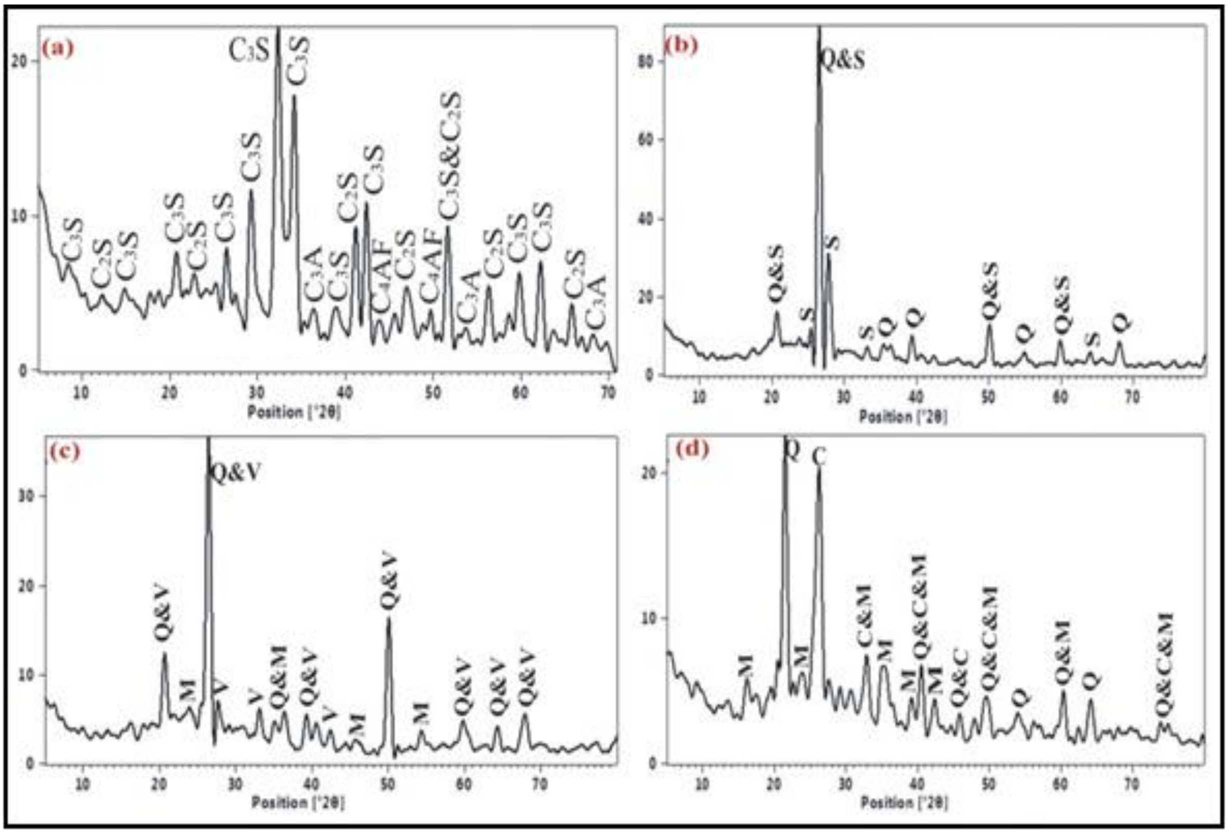

Fig.2. XRD patterns of clinker (a) (WFCBs) (b) (WCTs) (c) (WVCPs) (d) Q: quartz (SiO2) C3S: Alite. C2S: Belite, C3A: Aluminate, C4AF: Ferrite, M: mullite (Al2O3.SiO2), S: sanidine (K Al Si3O8), V: vaterite (CaCO3), C: cristobalite (SiO2).

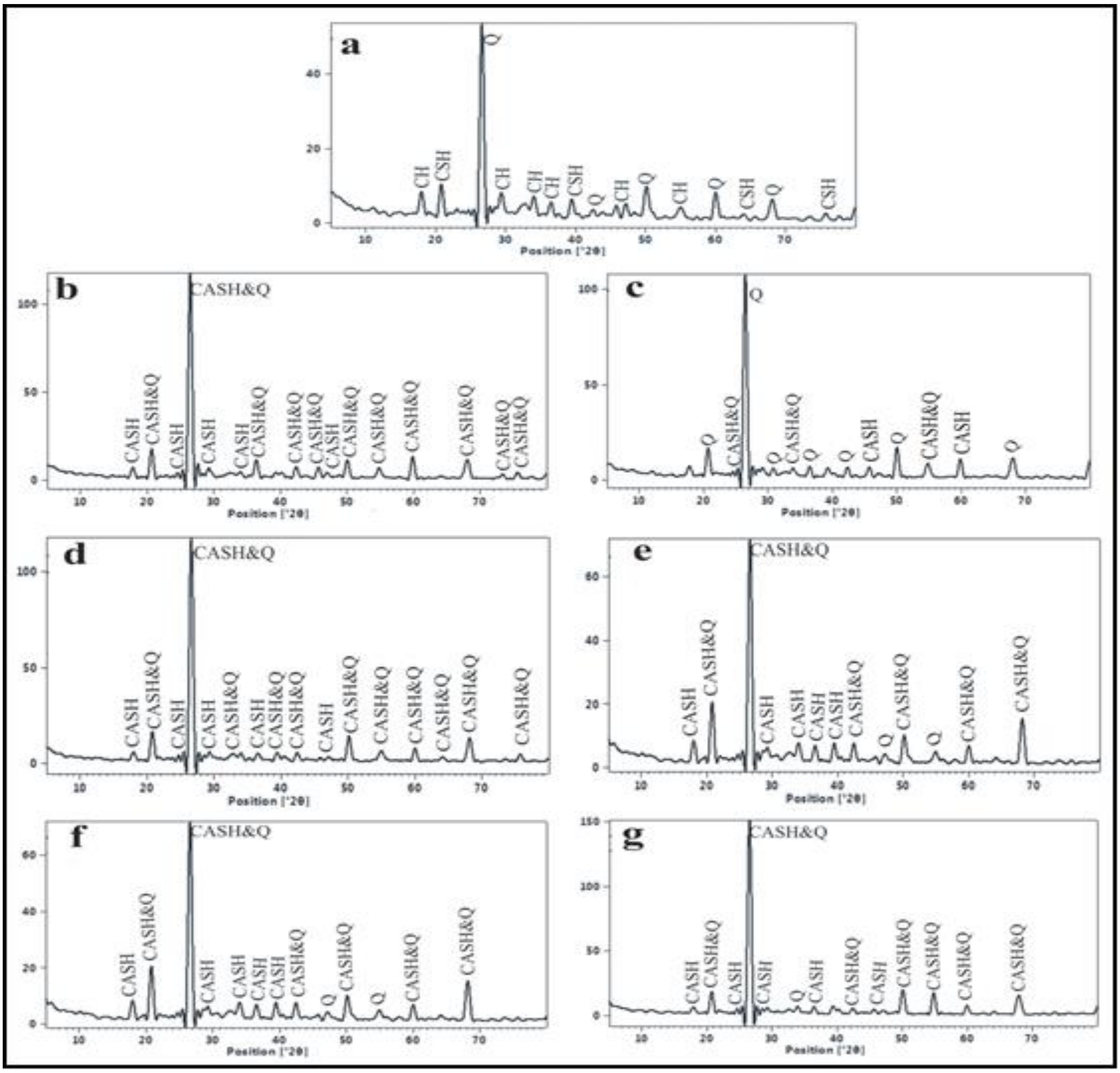

Fig.3. XRD patterns of hardened mortar specimens cured for 28 days, blank mortar (a) 10 Wt.% (WFCBs) (b) 20 Wt.% (WFCBs) (c) 10 Wt.% (WCTs) (d) 20 Wt.% (WCTs) (e) 10 Wt.% (WVCPs) (f) and 20 Wt.% (WVCPs) (g). Q: quartz, CH: portlandite, CSH: Calcium silicate hydrate (tobermorite), and CASH: calcium aluminate silicate hydrated.

Whereas the broad exothermic peaks effect ranges from 630 Cº to 750 Cº is referred to as calcination of calcium carbonate. It is companied with a remarkable loss of mass about 7.6, 5.6, 6.7, 7.5, 8.2, 5.8, and 6.2(%) for C.0, C.1, C.3, C.5, C.7, C.9, and C.11 respectively. The results reflect that the peak field and content of portlandite (CH) of all the studied blended cement mortars is smaller than the blank mortar. It is a result of pozzolanic reactions between studied wastes and cement matrix leading to (CH) consumption (Eloy *et al*., 2020; Anjaneya *et al*.,2021).

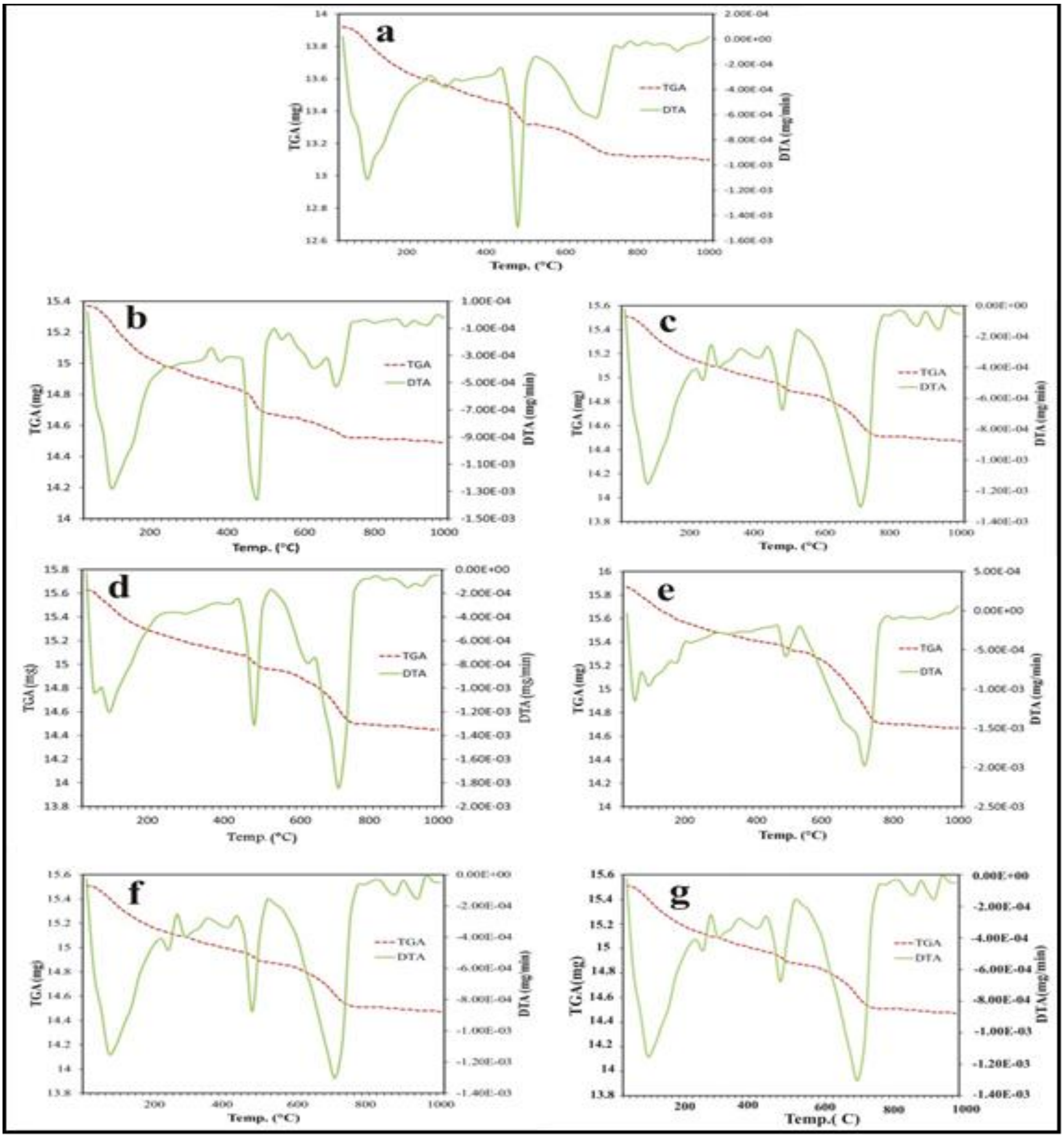

Fig.4. DTA and TGA thermograms of mortar specimens cured for 28 days, blank mortar (a) 10 Wt.% (WFCBs) (b) 20 Wt.% (WFCBs) (c) 10 Wt.% (WCTs) (d) 20 Wt.% (WCTs) (e) 10 Wt.% (WVCPs) (f) and 20 Wt.% (WVCPs) (g).

SEM of the studied materials and hardened blended cement mortars

The microstructure of the used materials and some selected 28 days cured hardened blank mortar specimens and blended cured cement mortar specimens (C.0, C.1, C.3, C.5, C.7, C.9, and C11) are shown in figures (5 and 6) respectively. The compounds and quality of the clinker samples can be investigated carefully using the energy dispersive x-ray spectrometry technique (EDAX) to establish the chemical composition and semi-quantitative distribution of the distinguished minerals in the clinker samples (Wickert, 1984). The microstructure of the studied clinker sample tested by SEM Figure (5a) reveals that the main phases are alite (hexagonal crystal), belite phases (rounded grains in clusters form), and the interstitial phases of aluminate and ferrite phases (irregular to lath-like crystal shape). The irregular shape, porous surface, and rough texture can be observed in the studied industrial waste materials (Fig. 5b-5d). Hematite appears as a pseudo-cube, mosaic texture, and irregular randomly oriented crystal form. Quartz is an angular roughly crystal form (Depeng *et al*., 2022). Cristobalite is the octahedral crystal form of fused silica. Mullite is an elongated acicular prismatic crystal form (Farouk *et al*., 2019; Lee *et al*., 2008). The SEM micrographs of the investigated blank hardened mortar and some selected hardened blended cement mortar specimens (C.0, C.1, C.3, C.5, C.7, C.9, C11) treated for 28 days (Fig. 6) illustrate that quartz and hydration phases, of ettringite crystal as needle-like form, amorphous products (CSH-gel), CH portlandite (elongated hexagonal crystals). In all investigated blended cement mortars, portlandite, and free lime consumed CASH formation (like honeycomb texture). That may be owing to the pozzolanic reaction between the expense of industrial waste materials and CH (Awoyera *et al*., 2017, Shigeta *et al*., 2018, Franus *et al*., 2015; Kunal *et al*., 2016; Myers *et al*., 2015). The low Ca/Al ratio for prepared blended cement compared to OPC contributed to the formation of CASH (Guangxiang *et al*., 2023). XRD and TGA data match with SEM results. The EDX analyses indicate that the addition of these pozzolanic materials in all mortar leads to the increase of Si and Al peaks especially by the increase in the (10-25%) substitution level compared to the blank mortar specimen.

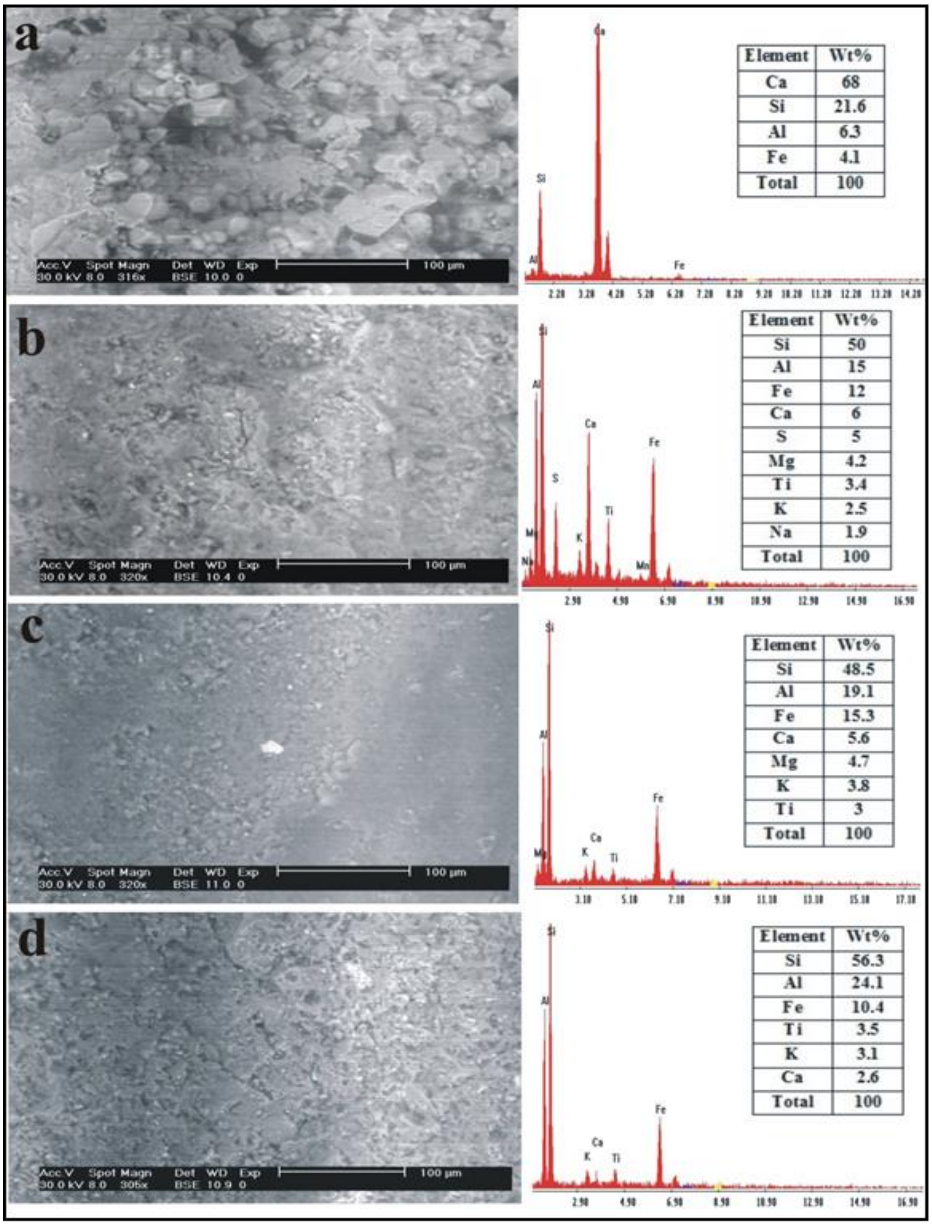

Fig.5. SEM micrographs show microstructure (a) clinker; (b) (WFCBs); (c) (WCTs); (d) (WVCPs) and its EDX spot micro-analyses

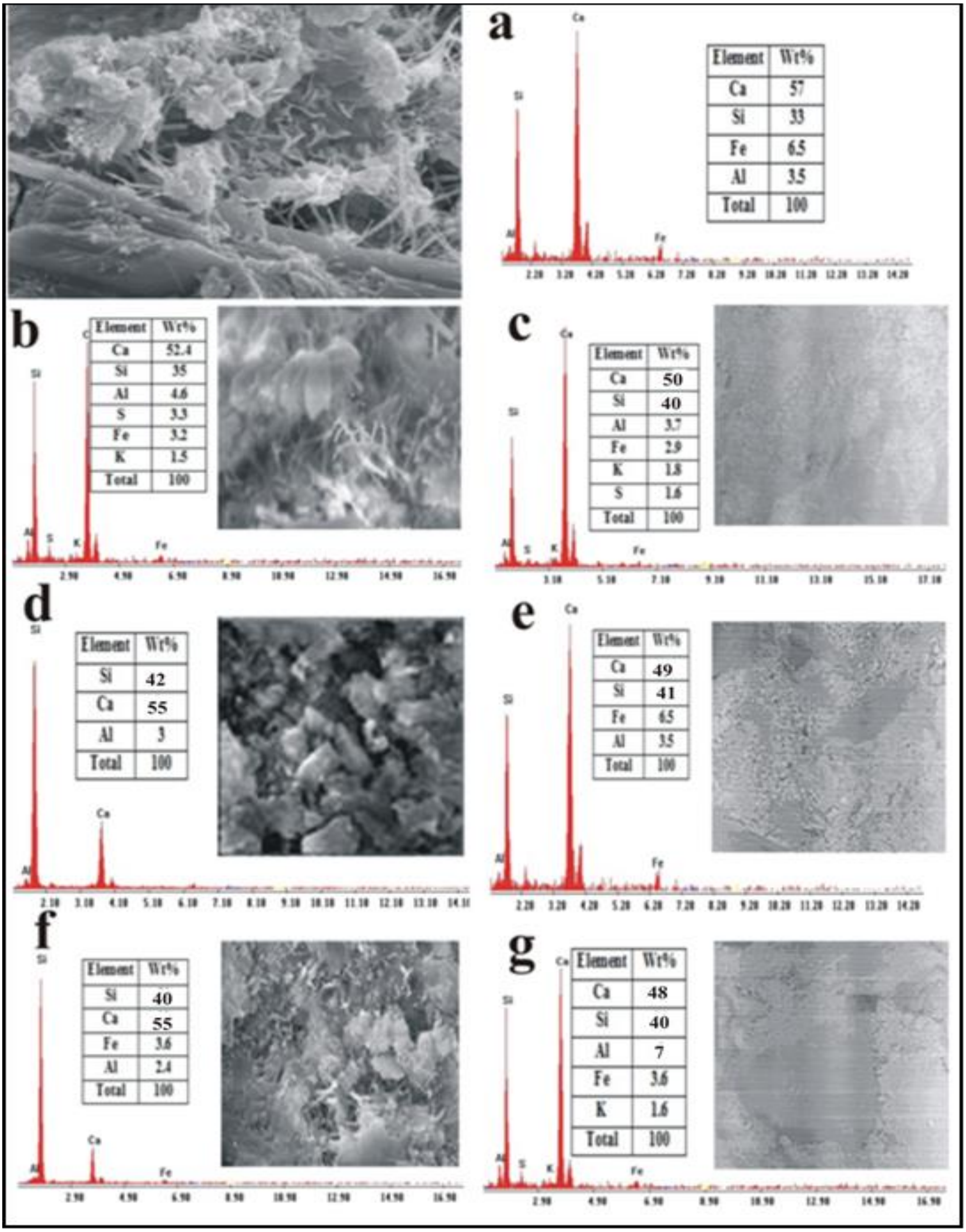

Fig.6. SEM micrograph shows the microstructure of hardened cement mortars cured for 28 days (a) blank, (b) 10 Wt. % (WFCBs); (c) 20 Wt.% (WFCBs), (d) 10 wt.% (WCTs), (e) 20 wt.%(WCTs), (f) 10 wt. % (WVCPs), (g) 20 wt. % (WVCPs) and its EDX spot micro-analyses

Phyco-mechanical properties of the studied cement pastes and hardened blended cement mortar specimens

The setting time of blank and blended cement pastes and water of consistency are given in table (4). The water consistency increased with the increasing replacement ratio of clinker by industrial wastes. Also, the setting times of the blended cement paste increase with the waste replacement ratio. Occasionally, the replacement of clinker with clay industrial wastes delays the setting time of cement. This is a result of the little pozzolanic behavior of studied waste at the early time of curing (Taha *et al*., 1981). These wastes possess high concentrations of SiO_2, Al_2O_3, Fe_2O_3, K_2O, and Na_2O compared to clinker (Hamdy *et al*., 2011). The increasing water consistency of the studied industrial waste materials powder may be due to their active surface area. The porosity is reduced by the filling of some pores by hydration products (Hamdy *et al*., 2011 Kae *et al*., 2010). The added water is increased with the increase of waste amount, so the setting times are increased (Marangu *et al*., 2018). The average strength results of the prepared 7 and 28 days cured specimens (Table .1) with replacement ratios of (10, 15, 20, and 25 wt. %) for the clinker cement (Table .4) revealed a significant gradual decrease in the compressive strength with increasing the replacement ratio of the studied industrial waste materials. These results match several published data such as (Peng *et al*. 2022; Bahforouz *et al*. 2020; Vejmlkova *et al*. 2014; Heidari *et al*. 2013). The highest value of the compressive strength (C5 = 40.5 MPa) is recorded with the replacement ratio of 10% WCTs and the lowest value of compressive strength (C12 = 33MPa) is noticed at a replacement ratio of 25% for WVCPs. At the late age of curing at 28 days, the compressive strength of blank mortar is greater than all studied hardened blended cement mortars, and mortar containing 10% (WCTs) has a higher value (C5 = 54.9 MPa) comparable to the lower value that recorded in a mortar containing 25% (WCTs; C7 = 43 MPa). These results match those of Juarez *et al*. (2021) and Chania *et al*. (2017). The flexural strength, specimens that contain 10% (WCTs; C5 = 9.8 MPa) have higher flexural strength at the later stage of curing at 28 days compared to the blank mortar (Cailos *et al*., 2020). It can be noted that the compressive strength value of mortars is proportionate to their flexural strength, where the higher flexural strength is related to the higher compressive strength. The SAI strength activity index is defined as the ratio of the compressive strength value of blended cement mortar including a pozzolana, divided by the compressive strength value of a blank cement mortar, where subjected to the same curing conditions according to ASTM (C0311-11B). The SAI increases with decreasing replacement ratio and enhances with increasing curing time. Except for the mortar replacement level of 25% (73%) from WCTs, and 25% (74.5%) from WVCPs, all replacement levels of the industrial waste in this study are similar to the strength index recognized by fly ash limitations greater than 75% of (Maria *et al*. 2016). The results show that the strength of blended cement mortar values came closer to the blank mortar (with no wastes) if the amount of dose from recyclable waste industrial materials is less than 10% wt. The recorded data displayed a rise in setting time leading to a rise in the compressive strength. Also, the compressive strength of prepared blended cement mortars is enhanced with increasing curing time.

Table 4. Physic-mechanical testing of the studied hardened blended cement mortars

Mix No.	Initial setting time (min.)	Final setting time (hr.)	Water Consis-tency%	Average Strength (MPa)				SAI% ≥ 75 % At 28 days
				7days		28days		
				Flexural	Compressive	Flexural	Compressive	
C.0	85	140	26	9	46.8	10.3	58.4	100
C.1	112	155	27.6	8	40.2	9.2	54.3	93
C.2	113	157	27.2	7	38.7	8.1	50.5	86
C.3	114	159	27	6.8	36.3	7.5	48.9	83
C.4	116	162	26.8	6.4	34.4	7.2	46	78
C.5	125	190	26.8	8.3	40.5	9.8	54.9	94
C.6	120	180	27	7.1	37	9	50	85
C.7	105	170	27.2	7.7	35.2	8.2	45.5	77
C.8	100	165	27.5	6.3	32.8	7.7	43	73
C.9	105	150	26.8	8.5	39.5	9	52.9	90.5
C.10	112	160	27	7.6	37.9	8	49.8	85
C.11	120	170	27.3	7.1	35.8	7.5	46.9	80
C.12	128	180	27.8	6.1	33	7.1	43.5	74.5

(SAI %) Strength activity index (ASTM C311/C311M-22).

Conclusions

Nowadays, the development of recyclable materials as raw materials in the cement industry as well as the studied materials in the Egyptian emerging economy is facing many challenges, such as these varying resources, chemical, mineralogical composition, and industrial processes. These industrial wastes require more efforts from researchers, technical centers, and current policies, strategies, and laws from governments to stimulate their reuse.

Based on the laboratory investigations and the obtained data it can be concluded that:

1. The studied industrial clay wastes have a potential use for producing pozzolanic blended cement. These wastes have chemical and mineral compositions that are suitable for reacting with portlandite to form cementing compounds (CASH) by the pozzolanic reaction.
2. Utilization of the investigated industrial wastes as recyclable materials from blended cement contributes to the mitigation of CO_2 footprint as an environmental concern, cost reduction of cement production as a financial concern, and the preservation of natural resources of the cement industry as a social concern.
3. The compressive strength of the studied blended cement mortars came closer to the blank cement mortar (with no wastes) with recyclable materials less than 10%.
4. The studied wastes lack waste management in terms of limiting their quantities, collecting them at a collection point, defining, classifying, sorting them chemically, and treating them mechanically, i.e., reducing their sizes to conform to cement, concrete, and construction codes, transporting them to factories, and providing continuous supply to cement factories.

Acknowledgments

The authors are appreciative to the laboratory teams of El-Arish Cement Company (ArCC) and Sinai Cement Company (SCC), for reporting the mechanical and physical tests for blended cement. Laboratories teams of the Nuclear Materials Authority (NMA) are kindly acknowledged for their help with the XRFandSEM-EDX measurement.

References

Adel, M., Medhat, S.E., Randa, A.O., Ibrahim, H.E., 2022. Potential Use of the Red Clay Bricks Production. Egyptian Journal of Applied Science Egyptian Paleozoic raw building materials at Abu Darag area Gulf of Suez for the f37(1_2). DOI 10.21608/EJAS.2022.232805.

Alp, I., Deveci, H., Süngün, Y.H., Yilmaz, A, O., Kesimal, A., Yilmaz, E., 2009. Pozzolanic Characteristics of Natural Raw Materials for Use in Blended Cements. Iranian Journal of Science and Technology, 33, 291-300.

Anjaneya, D., Hongjian, D., Sze, D., P., 2021. Performance of Mortar Incorporating Calcined Marine Clays with Varying Kaolinite Content. Journal of Cleaner Production, 265 (2021) 124513. https://DOI.org/10.1016/j.jclepro.2020.124513

ASTM (C349-18). Standard Test Method for Compressive Strength of Hydraulic Cement Mortars (Using Portions Prisms Broken in Flexure). DOI:10.1520/C0349-18.

ASTM (C348-21). Standard Testing Method for Flexure Strength of Hydraulic Cement Mortars. DOI:10.1520/C0348-21.

ASTM (C0311-11B). Standard Testing Method for Sampling and Testing Fly Ash or Natural Pozzolans for Use in Portland-Cement Concrete. Strength Activity Index with Portland Cement 27-30. DOI:10.1520/C0311-C0311M.22.

Awoyera, P.O., Akinmusuru, J.O., Moncea, A., 2017. Hydration Mechanism and Strength Properties of Recycled Aggregate Concrete Made Using Ceramic Blended Cement. Congent Engineering, 4(1), 1282667. DOI 10.1080123311916.2017.1282667.

Barbara, L., Pawel, D., Klaartje, D.W., 2016. Thermogravimetric Analysis. Karen, S., Ruben, S., and Barbara, L., (Eds). A practical guide of microstructural analysis of cementitious materials. CRS Press, Boca Raton, pp. 177-211.

Behforouz, B., Memarzadeh, P., Eftekhar, M., Fathi, F., 2020. Regression and ANN Models for Durability and Mechanical Characteristics of Waste Ceramic Powder High Performance Sustainable Concrete. Computer and Concrete, 25(2), pp. 119-132. DOI:10.12989/cac.2020.25.2.000

BSEN 196-3. Methods of Testing Cement, Determination of Setting Times and Soundness. https:/DOI:110.3403/30338529U.

BS 8615-1:2019. Specification for Pozzolanic Materials for Use with Portland Cement, Natural Pozzolana and Natural Calcined Pozzolana.

Cailos, H, A., Cèsar, P., Rafael, T., 2020. Portland Cement with High Content of Calcined Clay: Mechanical Strength Behavior and Sulfate Durability Materials, 13(18):4206. DOI:10.3390/ma13/184206.

Chania, N., Yacine, C., Soraya, N., 2017. Characterization of Eco-Substituted Cement Containing Waste Ground Calcined Clay Brick. Canadian Journal of Civil Engineering. V.44. https://DOI.org/10.1016/cjce-2016.0537.

Cheng, H.L., Tian, H.Z., 2014. The Research of Potential Activation on Waste Clay Brick. J Recycling research (in Chinese), 11: pp. 25-27.

Commit, A.C.I. 232, 1994. Use of Natural Pozzolana in concrete 91, 410 P.

Dapeng, Z., Xinwen, L., Hongzhi, C., Waiching, T., Wei, L., Ding. Z., 2022. Study of Performances and Microstructures of Mortar with Calcined Low-Grade Clay. Construction and Building Materials 327 (2022) 126963. https://DOI.org/10.1016/j.conbuildmat.2022.126963

Darweesh, H.H.M., 2017. Firing Resistance of Ordinary Portland Cement Pastes Incorporated a Waste of Building Bricks. American Journal of Chemical Engineering; 5(6): 140-146. DOI: 10.11648/j.ajche.20170506.14.

El-Desoky, H.M., Farouk, S., Heikal, MA.H., El-Mahallawi, M., Wahid, A., 2019. Geochemical and Technical Investigation of some Clay Materials in the Industry. Journal of African Earth Sciences Volume 160, December 2019, 103612. https://DOI.org/10.1016/j.jafrearsci.2019.103612.

Eloy, A., Cèsar, M., Moisès, F., María, I.S.R., 2020. Fired Clay-Based Construction and Demolition Waste as Pozzolanic Addition in Cement. Design Eco-Efficient Cements. Journal of Cleaner Production, 265 (2020) 121610. DOI: 10.1016/j.jclepro.2020.121610

Ewa, T., Stepkowska, J.L., Pèrez, R., Maria, J.S., Jose, M.M.B., 2003. Calcite, Vaterite and Aragonite Forming on Cement Hydration from Liquid and Gaseous Phase. Journal of Thermal Analysis and Calorimetry 73(1): 247-269. DOI:10.1023/A:1025158213560.

Farouk, S., El-Desoky, H.M., Heikal, MA.H., El-Mahallawi, M., Wahid, A., 2019. Egyptian Cretaceous Clays Deposits: Insights on Mineralogy, Geochemistry, and Industrial uses. Arabian Journal of Geoscience (2020) 13:556. https://DOI.org/10.1007/s12517-020-05557-7

Franus, W., Pank, R., Wdowin, M., 2015. SEM Investigation of Microstructure in Hydration Products of Portland Cement. Speringer International Publishing Switzerland,2015, p.105. DOI.10.1007/978-319-16919-4-14.

Guangxiang, J., Hafiz, A. A., Keke, S., Dongxing, X., Xiaoqin, P. and Jingjun, L., 2023. Volume Deformation and Hydration Behavior of Ordinary Portland Cement/ Calcium Sulfoaluminate Cement blends. Materials, 16(7), 2652.https://DOI 110.3390/ma16072652.

Halblazig- Zig Kilns Technology, 2014 and 2019. The Brick Industry. http://www.hablakilns.com/industry.

Hamdy, E., Enas A., Randa, M.O., 2011. Fire Resistance of Fired Clay Bricks-Fly Ash Composite Cement Pastes. Ceramic International 38 (2011) 201-209. DOI: 10.1016/j.ceramint.2011.06.050

Han, T., Jin X.Z., 2015. Evaluation and Application of Waste Fired Clay Brick Renewable Gelled Material. J Researchand Application of building material (in Chinese),3 (2015), p.10-12

Heidari, A., Tavakoli, D., 2013. A Study of the Mechanical Properties of Ground Ceramic Powder Concrete in Corporating Nano-SiO_2 Particles. Construction and Building Materials, 38(9), 255-264. DOI 10.1016/jconbuildmat.2012.07.110.

Heikal, M., 2000. Effect of Temperature on the Physic-Mechanical and Mineralogical Properties of Homra Pozzolanic Cement Pastes. Cement and Concrete Research 30, 1835-1839. DOI: 10.4236/ojce.2018.81003.

Hewlett, P.C., Frederick, M., L., 1998. Chemistry of Cement and Concrete, 4th ed., John Wiley and Sons Inc., New York.

Juarez, H.F., Claudio, A.O.P., Oldair, D. L., Monica, R.G., Marcelo, H.F.M., 2021. Red Ceramic Waste as Supplementary Cementitious Material: Microstructure and Mechanical Properties. Construction and Building Materials. V.296, 2021, 123653. https://DOI.org/10.1016/j.conbuilmat.2021.123653.

Kae, L.L., Bor, Y.C., Chyow, S.C., 2010. Waste Brick's Potential for Use as a Pozzolan in Blended Portland Cement. Waste Management and Research 2010:28:647-652 DOI :10.1177/0734242X09355853

Kunal. K.P., Anfral, F.A., Mohmmed, F.A., Cheahuychou, M., Ali, B., Steven, D.P., Ora, B., 2016. Microstructure of cement paste with natural pozzolanic volcanic ash and Portland Cement at different stages of curing. Construction and Building Materials 113(2016). pp.423-441. https://DOI.org/10.1016/j.conbuildmat.2016.03.084.

Lee, V., Yeh, T., 2008. Sintering effects on the development of mechanical properties of fired clay ceramics. Mater Sci. Eng. 4855:5-13. https://DOI.org/10.1016/j.msea.2007.07.068.

Li SD., 2005. The feasibility of producing building materials products using construction waste. J Brick and tile (in Chinese), (12) :36-38.

Lin, K.l., Chen B.Y., Chiou, C.S., Au, C., 2010. Waste brich̓s potential for as a pozzolan in blended Portland cement. J waste management and research, 208(7): 647-652. https://DOI.org/10.1177/0734242X09355853.

Ma, CT., 2009. Experimental study on utilization regeneration of powder of construction waste. J. Ningixia engineering technology (in Chinese), 1(3):55-58. http://en.cnki.com.cn › CJFDTotal-NXGJ200901020.

Maria, A., Mas, J.M., Jordi, P., Luci, R., Maria, V.B., 2016. Ceramic tiles waste as replacement material in Portland cement. Advances in Cement Research, 28(4), 221-232. https://DOI.org/10.1680/jadcr.15.00021.

Marangu, M., Thionġo, K., Wachira, M., 2018. Properties of activated blended cement containing high content of calcined clay. Journal of Heliyon. Cell Press, v. 4. Issue 8,2018, e00742. https://DOI.org/10.1016/j.heliyon.2018.e00742

Massazza, F., 1993. Pozzolanic Cements. Cement and Concrete Composites, 15, 185-214. https://DOI.org/10.1016/0958-9465(93)90023-3.

Malinowski, R., Garfinkel, Y., 1991. Prehistory of concrete, Concrete International 13(3) 62-68.

Meyer, C., 2009. The greening of concrete industry. Cement and Concrete Composites, 31(8): 601-605. DOI: 10.1016/J.CEMCONCOMP.2008.12.010.

Mohamed, A.A., 2022. Performance and hydration characteristic of dark white evolution (DWE) cement composites blended with clay brick powder. Egypt. J. Chem. Vol. 65, No. 8, pp. 419 –427.

Mohamed, S.E., Ali, I.M.I., Basel, N.A.S., 2021.Utilization of some Egyptian raw materials in ceramic tiles. Silicon (2021) 13:985–992. https://DOI.org/10.1007/s12633-020-00459-5.

Murat., M., 1983. Hydration of reaction and hardening of calcined clays and reacted minerals: II. Influence of mineralogical properties of the raw-kaolinite on the reactivity of metakaolinite, Cement Concrete Res. 13(1983), 511-56-18.

Myers, R.J., L̕-̀Hôpital, E., Provis, J.L., Lothenbach, B., 2015. Effect of temperature and aluminium on calcium (alumino) silicate hydration chemistry under equilibrium conditions. Cem. Concr.Res.68,83-93.DOI:10.1016/j.cemconres.2014.10.015.

Naceri, A., Hamina, M.C., 2009. Use of waste brick as a partial replacement of cement in mortar. J WASTE Management, 29 (8):2378-2384. DOI:10.1016/j.wasman.2009.03.026

Oluwarotimi, O., Anthony, E., Julius, N., David, O., Precious, F., Cynthia, Ch., Kehinde, O., 2019. Reuse of pulverized fired clay brick wastes as cement substitute in mortar for sustainable construction. IOP Conf. Series: Materials Science and Engineering 652 (2019) 012048. DOI:10.1088/1757-899X/652/1/012048.

Peng, Z., Peishuo, Z., Jingjiang, W., Zhenhui, G., Ycng, Z., Yuanxum, Z., 2022. Mechanical Properties of Durability of Sustainable Concrete Manufactured Using Ceramic Waste: A Review. Journal of Renewable Materials. DOI: 1032604/jrm.2022.03290

Per, K., 2003. X-ray diffraction and scanning electron microscopy studied of calcium carbonate electrodeposited on steel surface. Colloids and surface A: Physicochemical and Engineering Aspects, Volume 212(1), p. 19-26. DOI:10.1016/S0927-7757(02)00296-0.

Ramachandran, V.S., Beaudoin, J.J., 1999. Handbook of Analytical Techniques in Concrete Science and Technology, Principles, Techniques and Applications, Noyes Publication, New York, USA, ISBN 0-8155-1437-9.

Reddy, B.V.V., Jagadish, KS., 2003. Embodied energy of common and alternative building materials and technologies, Energy Build. 35:129-137. DOI:10.1016/S0378-7788(01)00141-4.

Robert, H. B., 1929. Calculation of compounds in Portland cement. Industerial andEngineering Chemistry Analytical Edition 1929,1,4,192-197. DOI: 10.1021/ac50068a006

Sadek, D.M., Amin, Sh.K., 2018. Conformity of Blended Cement Incorporating Ground Ceramic with Cement Standards. European Journal of Scientific Research, pp. 265-276. https://www.europeanjournalofscientificresearch.com/issues.

Shigeta, A., Ogawa, Y., Kawai, K., 2018. Microscopic investigation on concrete cured internally by using porous ceramic roof-tile waste aggregate. MATEC Web of Conferwnce, 195,01004. DOI 10.1051/marecconf/201819501004.

Singh, N.B., Singh, Neelam., Rai, S., Singh, Namwar., 2001. Hydration of rice husk ash blended Portland cement. Indian Journal of Engineering and Material Science Vol. 8, pp. 235-238.

Siong K.L., Yee L.L., Ming K.Y., Wen W.N., Foo, W.L., Kok, Z.K., Jee, H.L., 2022. Mechanical Properties of lightweight Foamed Concrete with Ceramic Tile Wastes as Partial Cement Replacement Material. Sec. Construction Materials. https://DOI.org/10.3389/fbuil.2022.836362.

Soroka, J., 1979. Portland cement Paste and Concrete, 4th ed., Edward Arnold, London.

DOI - 10.1007/978-1-349-03994-47

Spence, R.I.S., Surkhi, M., 1974. Lime and Alternative Cement Proceedings of one day seminar on small scale manufacturing of Cementitious Materials, Intermediate Technology Development Group, London, pp. 18-21.

Taha, A.S., El-Didamony, H., Abo-Enein, S.A., Amer, H.A., 1981. Phyiso- Chemical properties of supersulfated cement pastes. Zement-Kalk-Gips, 34,315.

Toledo, F.R.D., Goncalves, J.P., Americano, B.B., 2007. Potential for use of crushed waste calcined-clay bricks as a supplementary cementitious material in Brazil. Cem. Conc. Res., 37, 1357-1365. DOI.10.1016/j.cemconres.2007.06.005.

Vejmelkova, E., Konakova, D., Kulovana, T., Hubacek, A., Cerny, R., 2014. Mechanical and thermal properties of moderate-strength concrete with ceramic powder used as supplementary cementitious material. Advanced Materials Research, 1054,194-198. DOI.10.4028/www.scientific.net/AMR.1054.94.

Viviana, F.R., Mònica, A.T., Alejandra, T., Claudia, C.C., Millena, P., Jarosly, P., Edgardo, F.I., Ondřej, J., Zbyšek, P., 2019. Complex Characterization and Behavior of waste Fired Brick Powdered-Portland Cement System. Materials, 12, 1650-1669. https://DOI.org/10.3390/ma12101650.

Wang, H., Zheng, L., 2012. Properties of concrete containing recycled clay brick powder. J Journal of Handing University (engineering science) (in Chinese), 2: 104-108. http://gxbwk.njournal.sdu.edu.cn/EN/Y2012/V42/I1/104.

Wickert, H., 1984. Cement course Materials Technology. By-Products of clinker burning: Kiln Dust and Stack Gas ″Holderbank″ Management and Consulting Ltd. Technical Center-Materials Division.

. Wild, S., Khatib, J.M., Sabir, B.B., Addis, S.D., 1996. Intcongr Concret in the Service of Mankind – Concret of Environment Enhancement and Portection, edited by R K Dhr and T D Dyer (Puplication E and Fn Spon, Dundee), p. 685-696. ISBN-13: 978-0419214502

Wu XM., 2004. Influence on physical and mechanical properties of cement with grinding construction waste powder as mineral admixture. J New building materials (in Chinese), 2004.4:16-18.

Yasong, Z., Jianming, G., Chuanbei, L., Xuemei, C., Zhenhai, X., 2020. The particle-size effect of waste clay brick powder on its pozzolanic activity and properties of blended cement. Journal of Cleaner Production, Volume 242, 1 January 2020, 118521. https://DOI.org/10.1016/j.jclepro.2019.118521.