**ENERGY PERFORMANCE AND CALORIMETRIC BEHAVIOUR OF CEMENTS BEARING
GRANITE SLUDGE. CONTENT FOR OPTIMAL PERFORMANCE**

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Abstract

Blending supplementary cementitious materials with portland cement is one of the current strategies for producing more eco-efficient binders by lowering the energy consumption and CO₂ emissions intrinsic to OPC manufacture. The effect of such additions on heat of hydration and energy performance is a subject of particular interest, for higher heat may reduce the service life of a concrete structure, whilst energy consumption per tonne of binder or megapascal may prove not to be energy-efficient. This paper explores the energy performance of granite sludge (GS) as an active addition to clinker and the effect of this by-product on heat of hydration and eco-efficiency. The findings show that maximum heating and total heat released are lower in the additioned than in the conventional material, with the difference widening at higher replacement ratios. Optimal energy performance is observed at ratios of 15 % to 30 % (both inclusive), with the experimental materials requiring less energy than ordinary cement per megapascal (MPa) of strength. Cements with 15 % to 30 % granite sludge are consequently eco-efficient. With 15 % GS they can be classified as ordinary, with 20 % to 30 % as low heat cements and with 35% as very low heat cements.

Keywords: heat of hydration, energy consumption, performance energy, cement, granite sludge

1. Introduction

At this time, approximately one-half of worldwide energy demand is generated by building construction, maintenance and conservation [1]. Cement, in turn, the most widely used binder in concrete, is known to be energy-intensive. Due to the high temperatures ($\approx 1450\text{ }^{\circ}\text{C}$) required for its manufacture, $\approx 12\%$ to $\approx 15\%$ of industrial energy consumption [2] and 10% of worldwide anthropogenic CO_2 emissions can be attributed to cement production [3]. One effective way to lower energy consumption in a structure's life cycle is to use eco-efficient materials, which carry a heavy weight in green construction evaluations. The materials and resources category in the LEED (Leadership in Energy and Environmental Design) certification system, for instance, accounts for 14% of the total score [4].

Against that backdrop, substances such as fly ash [5], granulated blast furnace slag [5], silicomanganese slag [6], ornamental stone sludge [7, 8] and fired clay-based waste [9, 10] have been used as supplementary cementitious materials (SCMs) in the cement industry or as concrete admixtures. The aim is to improve concrete mechanical strength and durability, lower heat of hydration and its release, reduce the clinker content in cement, lower CO_2 emissions and energy consumption in cement manufacture and reduce the construction industry's environmental footprint [11, 12].

Cement hydration is a highly exothermal process that raises early age concrete temperature, one of the critical issues in the design and construction of structures requiring vast volumes of bulk concrete, such as dams or dikes, where heat dissipation is limited. Early age cracking and premature distress in concrete structures is normally attributable to that temperature rise and the concomitant presence of thermal gradients inside concrete elements [13, 14].

Temperature gradients are primarily governed by concrete's low thermal conductivity, cement hydration, ambient temperature and element or member thickness [15, 16]. As concrete cures its surface cools, raising surface tension due to the significant temperature differences between its interior and exterior. More specifically, the internal temperature of bulk concrete in a dam may reach $50\text{ }^{\circ}\text{C}$ to $70\text{ }^{\circ}\text{C}$, prompting thermal stress and cracking [1] because the tension generated in the early hours is greater than concrete tensile strength. Cracking affords channels for the ready ingress of aggressive external agents that compromise a structure's durability [17]. Both economically speaking and from the standpoint of service life performance, one of the fundamental characteristics of cement-based materials such as concrete and mortar is the heat

of hydration released. It is of particular significance where additions partially replace cement to produce eco-efficient cements and concretes [18]. According to Nath et al. [19], approximately \$18 bn to \$21 bn (english billion) are spent yearly to repair, rehabilitate, strengthen and protect concrete structures.

The study of the effect of including new additions on both cement energy performance and heat of hydration is a novel approach to pursuing waste valorisation in the construction industry, an issue of particular interest to the scientific community. Whilst a number of studies have been conducted to establish the relationship between the pozzolanicity of such materials and heat of hydration [20, 21], none has dealt simultaneously with the effect of the partial replacement of cement with granite sludge on heat of hydration and energy performance in these new binders. This study attempts to deepen the understanding of the inclusion of 10 wt%, 15 wt%, 20 wt%, 25 wt%, 30 wt% and 35 wt% granite sludge as a partial replacement for clinker on hydration kinetics and energy performance in new eco-efficient cements. The waste used is characterised and the heat released by the new binders during hydration is determined with semi-adiabatic calorimetry. Their energy performance and mechanical behaviour are also evaluated.

2. Materials and experimental procedure

2.1. Materials

2.1.1. Granite sludge

The granite sludge used in this study was supplied by an ornamental granite quarry at Quintana de la Serena, Badajoz, in Extremadura, one of Spain's autonomous regions. The sludge is generated both when parallelepiped blocks are cut from the raw stone and when slabs of varying thicknesses and a wide spectrum of sizes are subsequently cut from the blocks. Water mixed with the granite dust is collected in ducts that empty into ponds where the sludge settles. When the ponds are full, they are emptied mechanically and the sludge is stockpiled in outdoor spoil heaps (Figure 1).

The sludge used here, taken from different heights of the pile to ensure the samples were representative, was collected in bins and dried to a constant weight in the laboratory prior to characterisation.

Figure 1. Granite sludge production

Further to the XRF-determined chemical composition of the sludge reported in an earlier paper [22], its majority components, SiO_2 (≈ 69 wt%) and Al_2O_3 (≈ 15 wt%), were found together with other oxides such as K_2O (≈ 4 wt%), Na_2O (≈ 3.5 wt%), Fe_2O_3 (≈ 2.5 wt%) and CaO (≈ 2.4 wt%). Granite sludge from other sources studied by Medina et al. [23] and Mashaly et al. [24] had a similar chemistry and in all cases exhibited >58 wt% SiO_2 and >11 wt% Al_2O_3 , along with >2.5 wt% alkalis ($\text{Na}_2\text{O} + \text{K}_2\text{O}$). The granite sludge used here had >22.4 wt% reactive silica, which is less than the 25 % minimum laid down in European standard EN 197-1 [25] for natural (P) or calcined (Q) pozzolans and fly ash. Mineralogically speaking, the waste contained alkaline feldspars, clays, mica, quartz and hematite, as reported in the aforementioned earlier study [22].

Sludge particle size was determined by laser diffraction. In Table 1 it is compared to the values observed by other authors for granite dust used as a partial replacement for cement in mortar and concrete design. The data show that in the material studied here 10 % of the particles were $<1.74 \mu\text{m}$; 50 % $<10.20 \mu\text{m}$ and 90 % $<40 \mu\text{m}$. The table also shows that the particle size distribution of the sludge used was similar to that reported earlier [24, 26], finer than observed by Li et al. [27, 28] and coarser than found by Elmoaty et al. [29].

Table 1. Particle size distribution in granite sludge

At $0.23 \text{ m}^2/\text{g}$ the Blaine specific surface of the waste was smaller than observed for agroindustrial additions ($0.27 \text{ m}^2/\text{g}$ to $0.49 \text{ m}^2/\text{g}$) [30] or some types of fly ash ($0.30 \text{ m}^2/\text{g}$) used as supplementary cementitious materials. It was likewise smaller than recorded for the CEM I 42.5 R cement used here ($0.34 \text{ m}^2/\text{g}$).

2.1.2. Other materials

The commercial CEM I 42.5 R (OPC) cement supplied by Lafarge, a Spanish cement manufacturer sited in the province of Toledo, contained at least 95 % clinker and ≤ 5 % minority components, as specified in EN 197-1 [25].

The standard sand used to manufacture the mortars had a silica content of >98 % and a maximum particle size of $<2 \text{ mm}$ [31].

By weight, the additioned cements were 10/90, 15/85, 20/80, 25/75, 30/70 or 35/65 blends of granite sludge (GS) and OPC, respectively labelled 10GS, 15GS, 20GS, 25GS, 30GS and 35GS.

The OPC and GS were blended in a shaker-mixer to ensure uniformity.

2.2. Methods

2.2.1. Activity index

Waste pozzolanicity was determined by finding the activity index. The procedure followed was similar to the one proposed in EN 450-1 [32] for fly ash used as an admixture in concrete manufacture.

A control mortar was prepared by mixing 1350 g of standard sand, 450 g of cement and 225 mL of distilled water in a planetary mixer for 5 min. The specimens prepared were de-moulded after 24 h and soaked in water at 20 ± 1 °C for 28 d. In the new binders, although part of the cement was replaced with granite sludge, the resulting mortars had the same consistency as the reference, with a tolerance of ± 5 mm. European standards recommend determining the activity index for replacement ratios of 20 %, whereas U.S. standards specify 25 %.

Compressive strength was then found for six specimens per mortar type and the mean represented as a percentage relative to the control mortar (AI), as in Equation 1:

$$AI = (\sigma_{\text{blended mortar}} / \sigma_{\text{control mortar}}) \times 100 \quad (1)$$

where: $\sigma_{\text{blended mortar}}$ is the compressive strength of the additioned mortars and $\sigma_{\text{control mortar}}$ is the compressive strength of the reference mortar, both expressed in MPa.

2.2.2. Cement chemical and physical characterisation

The mixes were characterised chemically on a Philips PW1404 (Amsterdam, Netherlands) X-ray fluorescence (XRF) spectrophotometer operating with a dual Sc/Mo anode X-ray tube. The rheological properties (initial and final setting times) for the new blended cements were determined using a Vicat needle, as described in European standard EN 196-3 [33]. The soundness of normal consistency cement paste was studied with a Le Chatelier instrument as specified in European standard EN 196-3 [33].

2.2.3. 3.7 Mortar mechanical strength

Early (2 d) and later (28 d) age, 4x4x16 cm mortar specimens were examined for flexural (three-point test) and compressive strength on an Ibertest Autotest-200/10-SW (Madrid, Spain) test frame. Mortars were mixed, moulded, de-moulded and cured as specified in European standard 196-1 [31].

2.2.4. Heat of hydration

Heat of hydration was calculated using the semi-adiabatic method (Langavant calorimeter) specified in European standard EN 196-9 [34]. In that method the heating recorded in the mortar studied is compared to that of an inert reference mortar (mixed 12 months prior) and the value found is entered into Equation 2 to determine heat of hydration (Q):

$$Q = \frac{C}{m_c} \theta_t + \frac{1}{m_c} \int_0^t \alpha \cdot \theta_t \cdot dt \quad (2)$$

where: where Q is heat of hydration (amount of heat released by the sample in $\text{J} \cdot \text{g}^{-1}$); m_c the mass (g) of the mortar tested; t (h) the hydration time; C ($\text{J} \cdot ^\circ\text{C}$) the total heat capacity in the calorimeter and the mortar tested; α ($\text{J} \cdot \text{h}^{-1} \cdot ^\circ\text{C}^{-1}$) the global thermal transmission coefficient; and θ_t ($^\circ\text{C}$) the difference between the calorimeter readings for the test and reference materials at time t .

Here the test was conducted on an IBERTEST IB32-101 Langavant calorimeter.

2.2.5. Energy performance of eco-efficient mortars

The method used, proposed by Hamidi et al. [35], is based on the energy consumed in cement manufacture (heating raw materials, burning the addition and clinkerisation) and grinding (clinker and granite sludge). The energy needed was calculated as shown in Equation 3:

$$E(\text{kW} \cdot \text{h}/\text{t}) = C \cdot (E_{\text{cement}}^{\text{process}} + E_{\text{cement}}^{\text{grinding}}) + \text{GS} \cdot (E_{\text{GS}}^{\text{process}} + E_{\text{GS}}^{\text{grinding}}) \quad (3)$$

where: E is the energy consumed to produce 1 t of binder; C the proportion of cement (1, 0.90, 0.85, 0.80, 0.75, 0.70 or 0.65); and GS the proportion of granite slag (0, 0.10, 0.15, 0.20, 0.25, 0.30 or 0.35); $E_{\text{cement}}^{\text{process}}$ and $E_{\text{GS}}^{\text{process}}$ are the energy consumed ($\text{kW} \cdot \text{t}/\text{h}$) in cement and GS manufacture, respectively; and $E_{\text{cement}}^{\text{grinding}}$ and $E_{\text{GS}}^{\text{grinding}}$ the energy consumed ($\text{kW} \cdot \text{t}/\text{h}$) in cement and GS grinding, respectively.

The values obtained from Equation 3 were then used to calculate mortar energy performance with Equation 4:

$$E_{\text{performance}}(\text{kW} \cdot \text{h}/\text{t} \cdot \text{MPa}) = \frac{E}{f_{cm}} \quad (4)$$

where: E is the energy consumed to produce 1 t of binder and f_{cm} is the compressive strength of the mortars studied.

3. Results and discussion

3.1. Chemical and physical properties

The XRF-determined chemical composition of the cements (Table 2) showed that the new cements met EN 197-1 chloride content, SO_3 content and loss on ignition (LoI) requirements for ordinary cements.

Table 2. Chemical composition of the cements studied

According to the initial and end setting times for the cement pastes at normal consistency (34 ± 2 mm) shown in Figure 2, the inclusion of 10 % to 35 % granite sludge accelerated hydration, which translated into slightly shorter initial and end setting times in the new cements. Nonetheless, that reduction did not compromise compliance with the initial setting time requirement laid down in standard EN 197-1 for strength class 42.5 MPa (≥ 60 min).

Figure 2. Initial and end setting time for the cements analysed

The difference in setting times widened with declining replacement ratio, with the initial time 30 % shorter in 10GS and 2 % shorter in 35GS than in OPC. As the behaviour observed was affected by different factors with opposite effects on rheology, initial setting time was not linearly related to replacement ratio. The factors favouring hydration include the filler effect initially induced by sludge, which contributes to cement aluminate (C_3A and C_4AF) and alite (C_3A and C_4AF) phase hydration [36]; and the presence of alkaline oxides (Na_2O and K_2O) in the GS, known to accelerate tricalcium aluminate phase (C_3A) hydration [37-39]. Other factors such as sludge TiO_2 content [40] and its smaller Blaine specific surface than OPC retarded hydration, however. The mitigation of acceleration with rising replacement ratios attests to the heavier impact of the retarding factors at increasing percentages of sludge content.

This tendency was also observed by Medina et al. [23], who studied 10 % to 20 % granite sludge in new cements, and Elmoaty et al. [29] in research on 5 % to 15 % granite dust in concrete.

Cement water demand, spread and expansion are given in Table 3. Water demand was found to rise with the replacement ratio, ranging from 2.2 % higher than OPC in 10GS binders to 5.8 % higher in 35GS materials.

Table 3. Physical properties of cements

The behaviour observed was directly related to the jagged, irregular edges of the granite sludge particles, as described in an earlier paper [22], which increase the amount of water required to fill the inter-particle space. These findings are consistent with observations reported by

Vijayalaskshmi et al. [41] and Mashaly et al. [24], who noted that particle surface texture, jaggedness and specific surface played a key role in water demand.

Including granite sludge in the cement used to prepare mortars at a constant water/cement ratio of 0.50 was found to reduce mortar fluidity by 7 % in 10GS and 18 % in 35GS. That observation was directly related to the higher water demand in the new cement pastes discussed above, along with waste morphology, which rendered the mortar more cohesive, rheologically speaking, due to its irregular shapes.

The data in Table 3 show that the partial replacement of cement with granite sludge had no expansive effect on the cement pastes, all of which met the EN 197-1 requisite (≤ 10 mm) [25].

3.2. Strength activity index

The 28 d strength activity indices (SAI) for the cements containing 20 % and 25 % additions, found with Equation 1, are shown in Figure 3. Although replacing the cement with the addition induced a decline in the activity index, the new binders exhibited 28 d SAI values greater than the 75 % requirement laid down in U.S. standard ASTM C618 [42] for cements with 20 % fly ash or natural pozzolans, and European standard EN 450-1 [32] for cements with 25 % fly ash. Further to those data and its chemical composition ($\text{SiO}_2 + \text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3 \geq 70$ %), granite sludge would meet the requirements laid down in those standards to qualify as a pozzolan.

Figure 3. Mortar activity index

These findings were similar to the 28 d strength activity indices recorded by Amin et al. [43] for cements including granite sludge waste (83.4 %), Davraz et al. [44] for andesite (76.5 %) and Vazzoler et al. [45] for ornamental stone waste (80 %). The activity index found here was smaller than for waste such as fired clay roof tiles with higher pozzolanicity: El-Dieb and Kanaan [46] found a 105 % AI for cement containing 20 % roof tile powder.

3.3. Mechanical strength

The 2 d and 28 d compressive and flexural strength values for the mortars studied (Figure 4) showed that all the mortars with a replacement ratio of 30 % or lower had a 2 d compressive strength of at least 20 MPa (42.5 R) and a 28 d strength of at least 42.5 MPa (42.5 R). They consequently met the EN 197-1 mechanical requirements for ordinary 42.5 MPa cements. The cements bearing 35 % granite sludge, in turn, were compliant for strength class 32.5 R, with a 2 d compressive strength of 10 MPa and a 28 d strength of 32.5 MPa.

Figure 4. Mortar 2 d and 28 d compressive and flexural strength

Two-day mechanical strength relative to OPC also declined with rising replacement ratio, by 31 % for compressive strength and 50 % for flexural strength in mortar 35GS. That pattern was not as clearly visible in the 28 d materials. The explanation may lie in the type of effect prevailing at the two ages. In the 2 d materials the dilution effect predominated, due to the smaller volume of hydration product as a result of the lower clinker content, whereas with time that effect was offset by the pozzolanicity of the waste. As noted in a prior study [22], granite sludge exhibits low early age and moderate later age pozzolanicity.

The 28 d findings varied depending on the replacement ratio, which defined three stages or regions. In the first, with 10 % replacement, performance declined with inclusion of the waste. In the second, between 10 % and 15 %, mechanical strength rose slightly with replacement ratio. And in the third, with percentages of over 15 %, performance again declined with rising ratios. The formation of hydration product from the pozzolanic reaction between GS and portlandite offset the dilution effect of adding GS to the OPC more effectively at 15 % than at any other ratio. The same pattern was observed by Ekaterina et al. [47] when studying 5 % to 30 % granite sludge additions. Those authors recorded an initial decline in compressive strength (at <5 % replacement) followed by a rise (at ratios of 5 % to 10 %) and subsequent decline (10 % to 30 % replacement).

Figure 4 also shows that strength declined relative to OPC in all the GS-bearing mortars, although less steeply in the 28 d materials. More specifically, the decline in compressive strength was smallest at 15 % replacement (6 %) and greatest at 35 % (39 %). Those findings were consistent with other authors' observations [26, 43, 47, 48].

Flexural strength behaviour followed a similar pattern, with performance declining in the 28 d mortars by 10 % to 23 % for mortars 10 GS, 20GS, 25GS, 30GS and 35GS. In the mortar with the 15 % optimal replacement ratio, however, flexural strength was no lower than in OPC.

3.4. Heat of hydration

3.4.1. Heating

Heating is plotted against time in Figure 5 for all the mortars analysed, with a peak recorded at 15 h to 18 h, depending on the mortar. The heating curve comprised three stages: a first, from 0 h to 3 h; a second, from 3 h to 18 h; and a third or hydration stage, from 18 h to 120 h.

Figure 5. Heat of hydration in mortars versus time

i) First stage (0 – 3 h)

Two behaviours relative to OPC were observed in initial hydration (0-3 h), which took place in the first stage (Figure 5, enlarged insert): an increase in 10GS mortars, which reached 30 % after 3 h; and a gradual decline in heating at replacement ratios of 15 % or over (by 10 % in mortar 15GS and 34 % in 35GS).

The rise found for mortar 10GS was the result of the capacity of its filler effect and its early age (≤ 3 h) pozzolanicity [22] to offset the dilution induced by the lower C_3A and especially C_3S contents.

The decline recorded for replacement ratios of 15 % or over was due to the prevalence of dilution over the filler effect and pozzolanicity, as shown by the value of the decline in heating, which was lower than the replacement ratio.

That pattern for ratios of 10 % to 30 % countered the findings recorded by authors analysing hydration kinetics in cements with other additions, such as metakaolin [49], silica fume, [49], thermally activated dredging sludge [50], construction and demolition waste (C&DW) [51, 52] or sanitary ware rejects (SW) [52]. Such differences are primarily attributable to the higher pozzolanicity and finer particle size in the aforementioned additions, which would induce the formation of new hydration product ($\text{waste} + \text{Ca(OH)}_2 \rightarrow \text{gels}$) and accelerate hydration, given that the additions act as nucleation sites.

In contrast, the behaviour observed for the 35GS mortars was similar to that reported by Asensio et al. [51], who found less heating in mortars bearing over 30 % C&DW, where dilution was predominant, than in conventional mortars.

ii) Second stage (3 – 18 h)

The second stage of heating, illustrated in Figure 6, was defined as the time from which hydration accelerated in all mortars (≥ 3 h) through the time at peak heating (≤ 20 h). The figure shows the linear regression lines for the upward arm of the heating curve, the slopes of which define the heating rate.

Figure 6. Second stage (3 h to 18 h) mortar heating vs time (slope of line=heating rate)

The results showed that dilution prevailed over waste pozzolanicity, for the slope on the heating – hydration time curve declined with replacement ratio. That decline fit the line defined by Equation 5, with a correlation coefficient (R^2) of 0.935:

$$v_{heat} = -0.06 \cdot X_{GS} + 3.95 \quad R^2 = 0.935 \quad (5)$$

where: v_{heat} is heating rate in °C/h and X_{GS} is the granite sludge content in wt%.

Heating rate in the new mortars relative to the OPC value ranged from 0.91 for GS10 to 0.48 for 35GS. Asensio et al. [51] also observed heating rate in mortars with 10 % and 30 % C&DW to decline to 0.60 to 0.42 of the OPC value.

The linear relationship between peak heat and the time at peak heat versus the granite sludge content (Figure 7) clearly shows the steady decline in peak heating with rising replacement ratios, with values relative to OPC ranging from 5.50 % for mortar 10GS to 35.47 % for mortars 35GS. The decline for percentages of over 10 % was steeper than the ≈ 15 % [51, 52] or ≈ 23 % [51, 53] recorded for other mortars additioned at ratios of 20 % to 30 % with C&DW [51, 52], a recycled cement paste fine (RCPF) [53] or fired clay SW [52]. The differences observed were closely related to the lower pozzolanicity exhibited by granite sludge than C&DW or SW.

Figure 7. Peak heat and time at peak heat vs replacement ratio in mortars

The time at peak heat relative to the time in OPC rose with rising replacement ratios, from 1.63 % in mortar 10GS to 16.21 % in mortar 35GS. The effect of lesser and slower heating is beneficial, for one of the factors with the heaviest impact on cementitious matrix durability is the heat of hydration generated in the first 10 h to 20 h, because the low thermal conductivity of these matrices induces steep thermal gradients, particularly when large volumes of bulk concrete are involved.

iii) Third stage (18 – 120 h)

The third stage observed on the heat curve (Figure 5) began at 18 h and ran through 120 h, when heating was lower than 2 °C. In this stage, the dilution effect observed in the preceding phase was gradually offset by the pozzolanicity of the waste [22].

After 24 h, all the mortars exhibited less heating than the reference, with a difference of -4.41 % in mortar 10GS and -27.94 % in mortar 35GS. The percentage decline in heating was lower than the respective replacement ratios, attesting to the reaction between the waste and the portlandite (primarily) generated during silicate phase hydration. After 48 h all the mortars

exhibited greater heating than the OPC due to the increasing capacity of the waste to fix lime over time [22] and the exothermal nature of the pozzolanic reaction.

3.4.2. Heat of hydration

The heat of hydration against time (up to 120 h or 5 d) curves in Figure 8 are characterised by a very steep rise after 12 h in the mortars containing less than 30 % waste (OPC, 10GS, 15GS, 20GS and 25GS) and after 16 h in 30GS and 35GS. Heat of hydration subsequently increased more gradually, peaking at and flattening after 32 h in the mortars with ≤ 25 % waste and at 44 h in those with ≥ 30 % waste.

Figure 8. Total heat of hydration in mortars

As the replacement ratio rose, the heat released declined relative to OPC, with 120 h values 4.55 % lower in mortar 10GS and 24.20 % lower in 35GS.

That pattern was consistent with other authors' [54, 55] observations for early age, low pozzolanic activity mineral additions (fly ash), as well as for other more active additions such as fluid catalytic cracking catalyst FCC waste [56] and carbon tailings activated at 600 °C [57]. In the latter, at replacement ratios of 20 % or over heat of hydration declined due to delayed pozzolanic activity resulting from the shortage of portlandite in the mortars.

Figure 8 also shows that given the heat of hydration released at 41 h and further to EN 197-1 [25] specifications, 10GS and 15GS can be classified as ordinary cements; 20GS, 25GS and 30GS, with heat of hydration < 270 J/g, as ordinary low heat cements; and 35GS, with heat of hydration < 220 J/g as a special very low heat cement.

The linear relationship between percentage of waste and heat of hydration at time t is expressed in Equation 6:

$$Q_t = A \cdot X_{GS} + B \quad (6)$$

where: Q_t is heat of hydration at time t , in J/g; A is the slope of the linear curve; X_{GS} is the granite sludge content in wt% and B is a constant.

Table 4 gives the value of the elements in Equation 6 for hydration times 24 h, 41 h, 48 h, 70 h and 120 h.

The equations proposed in the table can predict the theoretical heat of hydration at time t in mortars with different replacement ratios, inasmuch as the regression obtained for seven points had a correlation coefficient of nearly 1. That same linear relationship was observed earlier by

Medina et al. [52] for mortars with 10 % and 20 % SW. Shanahan et al. [58] also proposed a linear model to predict heat of hydration in cements with other additions, such as fly ash and metakaolin.

Table 4. Regression equation values for the relationship between replacement ratio and heat of hydration released by mortars

3.5. Energy performance

Table 5 lists the values used to estimate the energy consumed per tonne of binder manufactured. The values for cement manufacture are well known [35, 59] and as GS needs neither to be thermally activated nor ground to a smaller size, its energy consumption is 0.

Table 5. Values used to calculate the energy consumed

The energy consumption (E) and energy performance (E_{fc}) versus replacement ratio graphs in Figure 9 show that including granite sludge induced a decline in energy consumption proportional to the percentage of GS. Hamidi et al. [35] observed the same pattern for andesite added to cement at rates of 10 % to 40 % and Saéz del Bosque et al. [61] in cements containing 10 % or 20 % slate sludge.

Figure 9. Energy consumption and energy performance in mortars

The cement containing 10 % granite sludge had 1.76 % lower energy performance than OPC in terms of E_{fc} , whilst 35GS exhibited a 6.43 % decline. The other four materials (15GS, 20GS, 25GS and 30GS), however, required less energy per MPa than OPC: mortar 15GS used 9.78 % less energy and mortar 30GS 5.05 % less.

The eco-efficiency of granite sludge-bearing mortars would be enhanced by CO₂ emissions abatement, with declines on the order of the replacement ratio, judging from other authors' reports for different SCMs: 20 % fly ash [62, 63] ($\Delta=-19.8\%/ -17.8\%$ CO₂ emissions); 35 % blast furnace slag [62] ($\Delta=-33.7\%$ CO₂ emissions); 20 % coal spoils burnt at 600 °C[59] ($\Delta=-12.0\%$ CO₂ emissions); and 10 % steel slag [64] ($\Delta=-9.5\%$ CO₂ emissions).

4. Conclusions

The conclusions that can be drawn from the present study are set out below.

- Cements containing granite sludge (10GS to 36GS) are EN 197-1-compliant in terms of chloride and sulfate content.

- Adding 10 % to 35 % granite sludge to cement paste shortens initial setting time relative to OPC, with the widest difference recorded for pastes with 30 % waste. Nonetheless, the new cements have no adverse effect on workability, as they meet the EN-197-1 minimum initial setting time requirement (≥ 60 min). These eco-efficient cements also comply with EN 197-1 soundness (≤ 10 mm) specifications. The strength activity index (SAI) in mortars 20GS and 25GS is higher than the 75 % required by standards ASTM C6818 for fly ash or natural pozzolans and EN 450-1 for fly ash.
- Mechanical strength is lower in the GS mortars than in OPC and declines with replacement ratio. Mortar 15GS exhibits the narrowest difference (6 %) and 35GS the widest (39 %). Cements with a replacement ratio of 30 % or under qualify for strength class 42.5 R, whereas the material with 35 % replacement meets class 32.5 R requirements.
- In the early hours of mortar hydration, heating is primarily impacted by the dilution effect induced by the replacement of cement with granite sludge.
- Mortar heating rate, largely governed by waste content, declines to 0.91 of the OPC value in mortar 10GS and 0.48 in mortar 35GS. In other words, the higher the percentage of waste, the longer it takes to reach maximum heating (slower hydration rate).
- Mortar peak heating values, reached at around 18 h, decline linearly with the percentage of granite sludge, by 5.50 % in mortar 10GS to 35.47 % in mortar 35GS.
- After 18 h of hydration, pozzolanicity begins to have a greater impact and after 48 h heating in the new mortars is greater than in those prepared with OPC.
- Heat of hydration declines linearly with replacement ratio. Materials 20GS, 25GS and 30 GS can be deemed low heat (< 270 J/g at 41 h) and 35 GS very low heat (< 220 J/g at 41 h) cements.
- New cements 15GS, 20GS, 25GS and 30GS exhibit higher energy performance than OPC, requiring less energy to produce cement with a given compressive strength.

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HIGHLIGHTS

- Energy performance of cements bearing granite sludge as an SCM assessed
- Heat of hydration in normal, low heat and very low heat blended cement analysed
- Mechanical performance of eco-friendly cement-based materials determined
- Effect of raw material replacement with waste on building sustainability discussed

Cutting granite into blocks

Sludge collection pond

Cutting blocks into slabs

Stockpiled granite sludge

Granite sludge removed from the pond

Stockpiled granite sludge

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Table 1. Particle size distribution in granite sludge

Granite sludge/dust	Maximum particle size (µm) by sample fraction		
	10 %	50 %	90 %
This study	1.74	10.29	40.38
Mashaly et al. [24]	1.92	11.42	50.00
Li et al. [27]	3.70	21.40	66.00
Li et al. [28]	4.60	20.50	53.50
Ramos et al. [26]	1.55	13.05	55.46
Elmoaty et al. [29]	2.00	15.00	27.00

Table 2. Chemical composition of the cements studied[illegible]

Table 3. Physical properties of cements

Property	Cement						
	OPC	10GS	15GS	20GS	25GS	30GS	35GS
Water demand (g)	156.0	159.5	160.0	163.0	164.0	164.0	165.0
Consistency (mm)	171.5	159.5	157.8	156.3	148.3	143.3	140.3
Expansion (mm)	1.0	1.0	1.0	1.0	1.0	1.0	1.0

Table 4. Regression equation values for the relationship between replacement ratio and heat of hydration released by mortars

Hydration time (h)	Elements in Equation 6		
	A	B	R ²
24	-3.14	309.85	0.973
41	-2.71	313.68	0.985
48	-2.59	312.50	0.983
70	-2.44	311.26	0.985
120	-2.30	313.27	0.984

Table 5. Values used to calculate the energy consumed

Process	Energy consumed [ref.]	
	Cement	Granite sludge (GS)
Manufacture	$E_{cement}^{process} = 1039 \text{ kW} \cdot \text{h/t}^*$	$E_{GS}^{process} = 0 \text{ kW} \cdot \text{h/t}$
Grinding	$E_{cement}^{grinding} = 50 \text{ kW} \cdot \text{h/t}$ [35]	$E_{GS}^{grinding} = 0 \text{ kW} \cdot \text{h/t}$
Note. - *According to Hosten and Fidan [60], cement production consumes approximately 830 kWh/t to 1100 kWh/t, and according to Arribas et al. [59] and Sáez del Bosque et al. [61], 1039 kWh/t		