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Use of phosphogypsum in cementitious systems containing spent equilibrium catalyst (Ecat) as a supplementary cementitious material (SCM)

Utilização de fosfogesso em sistemas cimentícios contendo catalisador de equilíbrio gasto (Ecat) como material cimentício suplementar (MCS)

PAIXÃO, Roberta de Souza da[1*]; MATOS, Samile Raiza Carvalho[2]; ROSA, Bruna Souza[1]; BARBOSA, Luanne Bastos de Britto[1]; GONÇALVES, Jardel Pereira[1]

1 Department of Engineering and Structures, UFBA, Salvador, Brazil

2 Training Center for Territorial Development, UFSB, Teixeira de Freitas, Brazil

* Corresponding author: robertapaixao200@gmail.com

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Abstract
Ecat, generated by the petroleum industry, shows potential for use as a Supplementary cementitious material (SCM) due to its rich composition of Al2O3 and SiO2. Phosphogypsum (PG) can be applied as a residual source of calcium sulfate in cements, but its application as a setting regulator in systems containing Ecat is unexplored. This study investigates the influence of PG on the hydration and mechanical performance of cementitious pastes, as well as its viability in composite cements with Ecat. PGs from different origins (SP and MG) were evaluated at levels of 0, 4, 8, and 12%, replacing natural gypsum; the level with the best performance was selected for the formulation with Ecat. Isothermal calorimetry, compressive strength, and XRD tests were performed. The addition of 4% PG provided balanced hydration and greater mechanical strength, while higher levels reduced the maximum heat flow and mechanical performance. The absence of sulfate accelerated hydration and increased the initial heat release. Systems with 50% Ecat exhibited a longer induction period, lower heat flux, and reduced resistance, with greater ettringite formation and portlandite consumption. Thus, performance depends on the balance between sulfate and SCM, making it feasible to incorporate optimized levels.
Keywords: Residual sulfate, Phosphogypsum, Supplementary cementitious material, Equilibrium catalyst, Hydration kinetics

Resumo
O Ecat, gerado pela indústria de petróleo, apresenta potencial para uso como MCS devido à sua composição rica em Al2O3 e SiO2. O fosfogesso (FG) pode ser aplicado como fonte residual de sulfato de cálcio em cimentos, porém sua aplicação como regulador de pega em sistemas contendo Ecat é inexplorada. Este estudo investiga a influência do FG na hidratação e no desempenho mecânico de pastas cimentícias, bem como sua viabilidade em cimentos compostos com Ecat. Foram avaliados FGs de origens distintas (SP e MG), nos teores de 0, 4, 8 e 12%, em substituição ao gesso natural, selecionando-se o teor com melhor desempenho para a formulação com Ecat. Foram realizados ensaios de calorimetria isotérmica, resistência à compressão e DRX. A adição de 4% de FG proporcionou equilíbrio na hidratação e maior resistência mecânica, enquanto teores superiores reduziram o fluxo máximo de calor e o desempenho mecânico. A ausência de sulfato acelerou a hidratação e elevou a liberação de calor inicial. Sistemas com 50% de Ecat apresentaram maior período de indução, menor fluxo de calor e resistência reduzida, com maior formação de etringita e consumo de portlandita. Assim, o desempenho depende do equilíbrio entre sulfato e MCS, sendo viável incorporar teores otimizados.
Palavras-chave: Sulfato residual, Fosfogesso, Material cimentício suplementar, Catalisador de equilíbrio gasto, Cinética de hidratação.

1 INTRODUCTION

The production of ordinary Portland cement accounts for approximately 8% of global carbon dioxide (CO_2) emissions, due to the decarbonation of limestone and energy-intensive manufacturing processes [1], [2]; reducing the clinker factor is one of the main strategies for mitigating these emissions in the cement industry [3]. In this context, the use of supplementary cementitious materials (SCMs) can help reduce carbon emissions associated with clinker production, decrease the use of non-renewable raw materials, and, at the same time, improve certain properties of concrete [4]. At the same time, the clinker grinding and cement production stages require the use of a sulfate source to control setting time [5].

Therefore, the integrated use of SCMs and alternative sulfate sources shows potential for application in the cement industry.

Fluid catalytic cracking (FCC) is a basic process for converting crude oil into refined products, using zeolite-based catalyst [6]. However, due to the formation of petroleum coke on their surface, these catalysts reach the end of their life cycle and are sent to landfills as general solid waste, known as spent equilibrium catalysts (Ecat), which poses serious environmental and health risks [6], since undesirable chemical contaminants can be released into the soil and water, while dust particles can be dispersed by the wind [7].

The composition and characteristics of Ecat vary depending on the refinery of origin and the type of catalyst processed [8]. However, it typically contains high concentrations of silica and alumina, which confer pozzolanic properties and offer potential for use as a cementitious material in cement matrices [9]. The pozzolanic properties of Ecat have been evaluated in previous studies [6], [8], [10], [11], [12]. In systems containing 10% cement replacement with Ecat (w/c = 0.5), compressive strength increased compared to the control at 14 and 28 days [10]. Furthermore, another study demonstrated an increase in compressive strength of up to 16.7% with cement replacements ranging from 10% to 20% (w/c = 0.30) [6]. Similar results were observed for an Ecat whose pozzolanic activity increased with the degree of substitution, with substitutions of up to 20% of the cement (w/c = 0.5) evaluated [11]. The production of phosphoric acid is responsible for generating a large amount of phosphogypsum (PG), a byproduct formed by the reaction of sulfuric acid with phosphate rock, widely used in the fertilizer industry [13]. It is estimated that, on average, 5 to 7 tons of PG are produced for each ton of phosphoric acid manufactured [14]. It is noteworthy that only about 15% of the phosphogypsum produced worldwide is recycled, reinforcing the need for strategies for its reuse in cementitious systems [15]. Replacing natural gypsum with phosphogypsum reduces the environmental impacts associated with its disposal, such as air, soil and groundwater contamination, as well as reducing the need for large disposal areas and the amount of natural gypsum extracted [16].

Calcium sulfate plays a fundamental role in controlling the hydration of the aluminate phase in cement, preventing instant setting and ensuring the necessary workability period [17]. Phosphogypsum has been considered an alternative source of sulfate [18], [19]. In its calcined form, phosphogypsum has been investigated as an alternative to gypsum in the formulation of calcined clay cements, such as LC^3 [3], [20], [21], in the production of calcium sulfoaluminate cement [22], [23], as a sulfate source in supersulfated cement [24], in the production of Portland clinker [25], and in the development of geopolymers [26]. When used in ternary cements, unprocessed FG demonstrated potential as an alternative source of calcium sulfate, providing adequate control of setting time and satisfactory mechanical performance, with strength exceeding 70% of that of Portland cement at 28 days [21]. Furthermore, the sulfate content proved to be a determining factor in the hydration kinetics, favoring the formation of ettringite over AFm phases and influencing the microstructure and strength of the cement [3]. In geopolymer systems, the incorporation of fly ash, slag, and alkaline activators also resulted in compressive strengths exceeding 60 MPa at 28 days, with the formation of dihydrate phosphogypsum, ettringite, and C-S-H gel associated with the development of strength [26].

Despite the potential for using phosphogypsum as an alternative source of sulfate, its use as a setting time regulator and its incorporation into cementitious systems containing Ecat have not yet been evaluated in the literature. In this context, this study aims to investigate the influence of phosphogypsum on the hydration kinetics and mechanical performance of pastes, as well as to evaluate its application as an alternative source of sulfate in the formulation of composite cements containing Ecat.

2 MATERIALS AND METHODS

2.1 MATERIALS

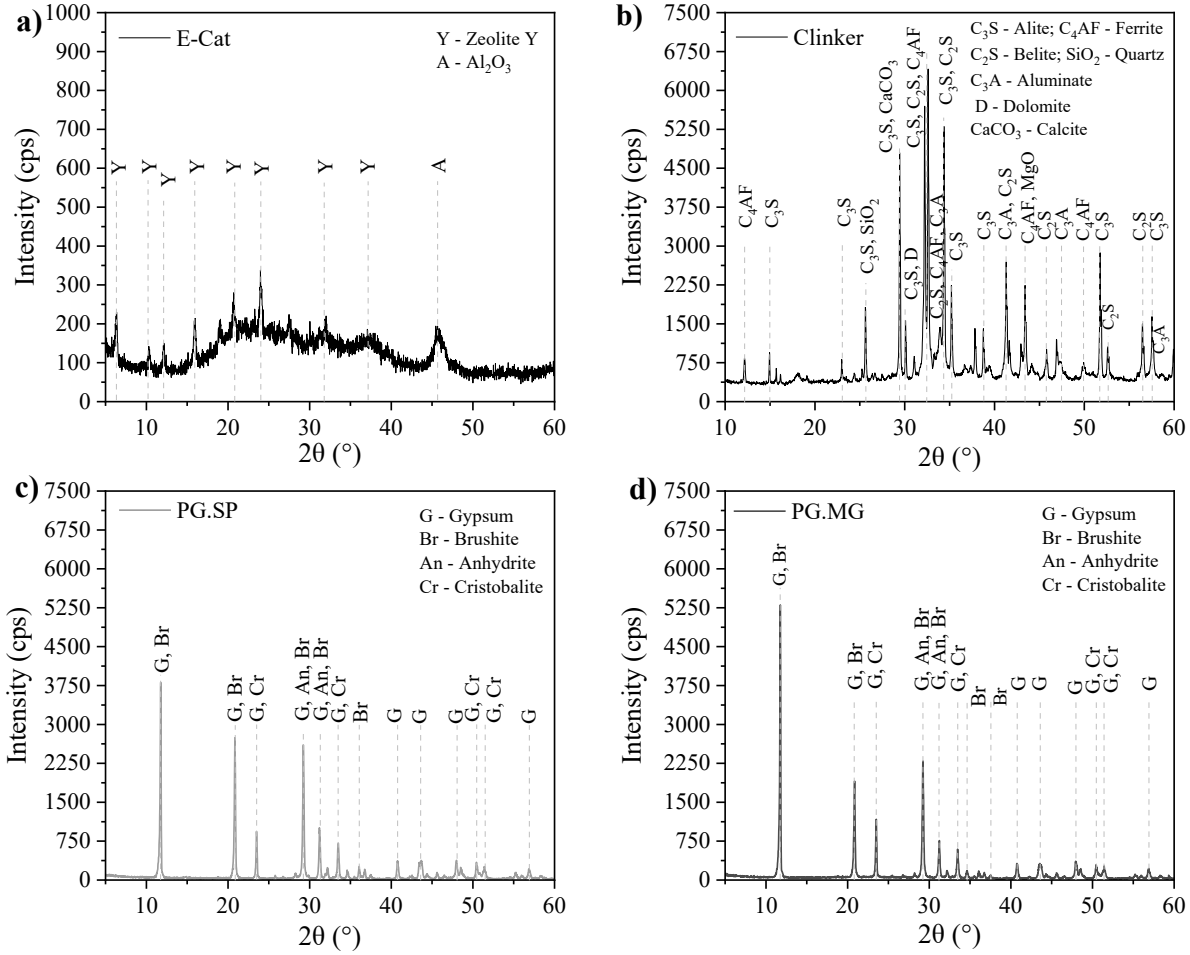
The materials used in this study were clinker, phosphogypsum (PG), and spent equilibrium catalyst (Ecat). The clinker was supplied by a cement plant located in the state of Sergipe, Brazil. It was first dried, ground, and sieved through a 75 μm sieve to ensure a homogeneous particle size distribution.

Analysis of the mineralogical phases, performed by X-ray diffraction (XRD), indicated that the clinker consisted primarily of C_3S (55.32%), C_2S (17.09%), C_3A (1.26%), and C_4AF (5.09%).

Two types of phosphogypsum from industrial fertilizer manufacturing plants located in the states of São Paulo (PG-SP) and Minas Gerais (PG-MG) were used as setting regulators; these were previously dried and ground.

Ecat, a waste product from fluid catalytic cracking units at a Brazilian refinery, was used as a supplementary cementitious material without additional heat treatment. The chemical composition of Ecat consists mainly of SiO_2 (46.9%) and Al_2O_3 (44.0%). The mineralogical phases identified in the raw materials are shown in Figure 1.

Figure 1: Diffractogram of raw materials: a) E-Cat, b) Clinker, c) PG.SP e d) PG.MG



2.2 EXPERIMENTAL PROGRAM

The experimental program was carried out in two complementary stages. Initially, the influence of phosphogypsum on the hydration and mechanical performance of clinker-based pastes was evaluated; in these pastes, natural gypsum was replaced by phosphogypsum at concentrations of 0, 4, 8, and 12% by mass, sourced from two distinct industrial origins (PG-SP and PG-MG). Based on the results obtained, the phosphogypsum content with the best performance was selected for use in the next stage.

In the second stage, the selected phosphogypsum content was used as a setting regulator in the formulation of composite cements containing spent equilibrium catalyst (Ecat) as a supplementary cementitious material (pozzolanic), in addition to reference systems containing analytically pure calcium sulfate ($CaSO_4$ P.A.).

2.2.1 Stage 1: Production of clinker pastes containing phosphogypsum

The mixtures were prepared based on a total mass of 100 g of solids, corresponding to the sum of the masses of clinker and phosphogypsum, in accordance with the previously established substitution levels. The amount of deionized water was determined based on a water-to-solids (w/s) ratio of 0.5. The components were mixed manually in a beaker using a spatula until a homogeneous paste with a uniform consistency was obtained; the paste was then subjected to tests to evaluate hydration and mechanical performance.

2.2.2 Stage 2: Production of composite cements

Experimental formulations of composite cements were developed, containing phosphogypsum as a setting regulator and a catalyst for the hydration equilibrium, used as a supplementary pozzolanic cementitious material, with SCM proportions compatible with the CPII-Z and CPIV types, in accordance with ABNT NBR 1669 - Portland Cement - Requirements [27]. The compositions adopted for CPII-Z and CPIV cements, considering the variation in phosphogypsum content and the use of the maximum Ecat (pozzolanic material) content permitted by the standard, are presented in Table 1. The phosphogypsum content used in each formulation was selected based on the best performance observed in Stage 1 of the experimental program. The homogenization of the composite cements was performed according to the procedures adopted by [28]. The samples were named based on the type of cement and the source of the phosphogypsum.

Table 1: Formulation of composite cements

Sample	Clinker (%)	Ecat (%)	*$CaSO_4$ (%)	PG-MG (%)	PG-SP (%)
CPIIZ-MG4	82	14	-	4	-
CPIIZ-SP4	82	14	-	-	4
CPII-REF	82	14	4	-	-
CPIV-MG4	46	50	-	4	-
CPIV-SP4	46	50	-	-	4
CPIV-REF	46	50	4	-	-
SE-REF**	96	-	4	-	-

*Analytical-grade calcium sulfate (A.G.); **Reference without Ecat

2.3 METHODS

2.3.1 Isothermal calorimetry

Isothermal calorimetry was used to evaluate the influence of phosphogypsum content on the hydration kinetics of cement pastes (Stage 1), as well as the effect of the phosphogypsum-Ecat interaction on the hydration process (Stage 2). The tests were conducted in an eight-channel TAM Air isothermal calorimeter (TA Instruments), with monitoring of heat flux and accumulated heat at 25°C over 48 hours (Stage 1) and 144 hours (Stage 2).

2.3.2 X-ray Diffraction (XRD)

XRD was used to identify the phases formed in the cement pastes at 28 days. To this end, the pastes were analysed using an XRD-6000 diffractometer (Shimadzu) with Cu Kα radiation at a wavelength of 0.154 nm. The X-ray tube was operated at 40 kV and 30 mA. The paste samples were manually ground into powders, all of which passed through a standard 75 μm sieve. The diffractograms were obtained over a range of 10 to 70° (2θ) with a step size of 0.02° and a scan rate of 2°/min. Phase quantification was determined using the Rietveld method with GSAS II software version 3913 [29] and the ICSD (*Inorganic Crystal Structure Database*).

2.3.3 Axial compressive strength

The axial compressive strength of the pastes was determined using cylindrical test specimens (2 x 4 cm). The specimens were tested at 28 days on a Zwick 1445 hydraulic actuator at a loading rate of 1 mm/min. The tests were conducted in triplicate, with the results expressed as the mean of the values obtained, accompanied by the respective standard deviation as a measure of dispersion. The test was used to compare the mechanical performance of the cementitious systems evaluated in the two stages of the study.

3 RESULTS E DISCUSSIONS

3.1 INFLUENCE OF PHOSPHOGYPSUM ON THE HYDRATION KINETICS AND MECHANICAL PERFORMANCE OF CEMENT PASTES

Figure 2 shows the heat release curves over the first 48 hours of hydration, allowing for an evaluation of the influence of the content of two different types of phosphogypsum on the behavior of the cement pastes. All samples exhibited typical exothermic behavior in the early stages, characterized by an initial peak associated with particle hydration, phase dissolution, and rapid aluminate reactions in the presence of sulfates. Subsequently, a main peak is observed, related to the acceleration phase of silicate hydration and the significant formation of C-S-H [30]. A previous study indicated that the higher the SO_3 content in the clinker, the less calcium sulfate needs to be added to produce cements with adequate hydration control [16]. In this context, the clinker used in the formulation of the evaluated pastes contains 2.8% SO_3, indicating a significant internal contribution of sulfate to the system and, consequently, a lower need for external addition to control the hydration kinetics. Analysis by isothermal calorimetry makes it possible to identify changes in hydration kinetics, particularly during the induction and acceleration phases, allowing for an evaluation of the role of phosphogypsum in regulating the system's initial reactions [31].

Cement is adequately sulfated when sulfate depletion occurs after the main peak associated with silicate hydration reactions [16]. However, in the systems analysed over a 48-hour period, this behavior was not observed. This result may be related to the fact that the analysis period was not long enough for the hydration reactions to progress to the point of sulfate depletion, or it may indicate a condition of subsulfation in the system (Figure 2). It is observed that the reference sample, composed of pure clinker, exhibited an extremely short induction period, practically non-existent, resulting in an almost immediate acceleration of the hydration reactions (Figure 2). This behavior is associated with the absence of sufficient sulfate to regulate the hydration of C_3A [32], which favors its rapid reaction with water and promotes intense heat release in the very first hours (3.21 mW/g_{solids}). As a result, setting occurs almost instantly, highlighting the importance of sulfate in modulating the initial kinetics of cementitious systems [17].

On the other hand, pastes containing phosphogypsum exhibited a prolonged induction period and a shift in the main hydration peak (Figure 2), indicating that the phosphogypsum content acts as a reaction regulator, providing greater control over the thermal evolution and setting time. For the 4% content, the peak was recorded at 5.4 h (SP4) with a maximum flux of 2.59 mW/g_{solids} and at 6.6 h (MG4) with 2.68 mW/g_{solids}, indicating a moderate prolongation of the induction period and control of C_3A hydration. At 8% content, a greater shift in the main hydration peak was observed, occurring between 6 and 7 hours, with a maximum heat flux of 2.53 mW/g_{solids} for PG.SP8 and 2.63 mW/g_{solids} for PG.MG8, evidencing an intensified retarding effect compared to the 4% content. For the 12% concentrations, the maximum heat release was recorded at approximately 7 hours, with values ranging from 2.4 to 3.0 mW/g_{solids}. PG.SP12 exhibited the lowest heat flux among the evaluated formulations (2.48 mW/g_{solids}). However, PG.MG12 exhibited a higher maximum heat flux (2.97 mW/g_{solids}), demonstrating distinct behavior even at the same addition level (12%) (Figure 2). Different to what has been observed in the literature, the increase in PG content did not cause the peak of the remaining C_3A hydration, observed in the reference sample, to shift to the right (Figure 2). This difference suggests that characteristics intrinsic to phosphogypsum sources, such as chemical composition, impurity content, and sulfate solubility, may influence the progression of hydration reactions and affect the sulfate balance [18].

Figure 2: Heat flow of composite cement mixtures over 48 hours of hydration (25°C)

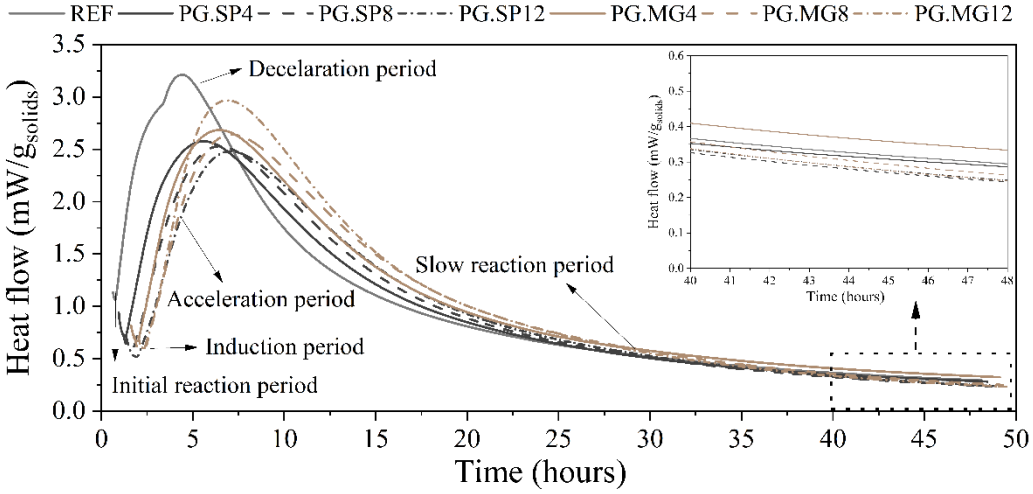
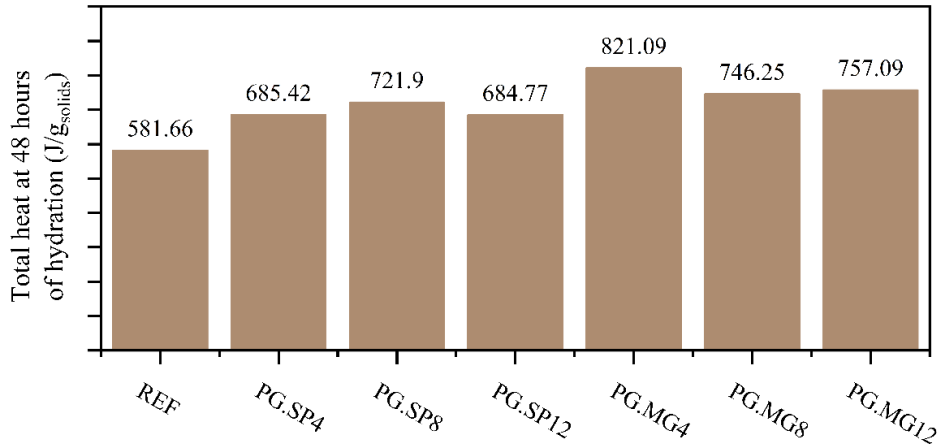


Figure 3 shows the cumulative heat of hydration over the first 48 hours. The reference sample exhibited a cumulative heat of 581.66 J/g$_{solids}$, while all formulations containing phosphogypsum showed higher values, indicating that the incorporation of phosphogypsum altered the hydration kinetics of the system. For PG.SP, an increase in cumulative heat was observed from 685.42 J/g$_{solids}$ at 4% replacement to 721.90 J/g$_{solids}$ at 8%, corresponding to increases of approximately 17.8% and 24.1% relative to the reference. However, with 12% PG.SP, the accumulated heat decreased to 684.77 J/g$_{solids}$, a value close to that observed for 4%, indicating that the increase in PG content did not result in a continuous rise in the heat released. For PG.MG, a 4% substitution resulted in the highest accumulated heat among all formulations, reaching 821.09 J/g$_{solids}$, approximately 41.2% higher than that of the reference formulation. At 8% and 12% replacement levels, values of 746.25 and 757.09 J/g$_{solids}$ were obtained, respectively, corresponding to increases of 28.3% and 30.2%. In this context, the results obtained in this study indicate that PG.MG had a greater influence on hydration under the evaluated conditions, particularly at the 4% substitution level, which exhibited the highest accumulated heat.

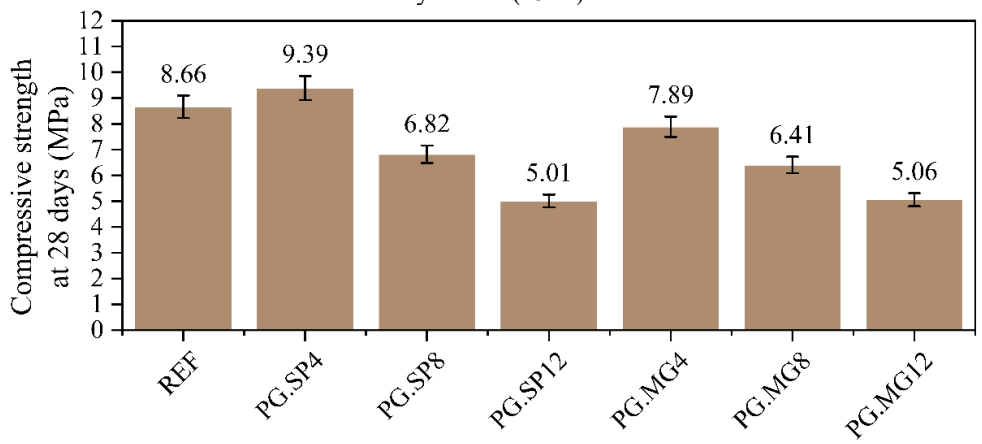
Figure 3: Total heat of the composite cement mixtures at 48 hours of hydration (25°C)



The effect of phosphogypsum content on the axial compressive strength of cementitious mixtures after 48 hours of hydration is shown in Figure 4. It can be observed that the reference sample (8.66 MPa), composed of pure clinker, performed worse than the PG.SP4 system, which achieved the highest strength value (9.39 MPa), demonstrating that the controlled addition of phosphogypsum can enhance the mechanical development of the material. However, increasing the content to 8% resulted in a decrease in strength, with values of 6.82 MPa (PG.SP8) and 6.41 MPa (PG.MG8), while a 12% content caused a more pronounced drop, reaching 5.01 MPa (PG.SP12) and 5.06 MPa (PG.MG12). This behavior indicates that the progressive increase in the phosphogypsum content, although it intensifies the regulating effect on hydration, may negatively affect the densification of the matrix. The analyses

show that the 8% and 12% phosphogypsum contents resulted in a reduction in compressive strength when compared to the reference sample, indicating that increasing the addition compromises the mechanical performance of the system. This behavior may be associated with a longer induction period (Figure 2). On the other hand, the 4% content provided adequate control of the hydration kinetics without compromising mechanical development, proving to be the most suitable proportion. Thus, considering the integrated analysis of thermal and mechanical behavior, the 4% content was selected for the formulation of CPII-Z and CPIV composite cements containing Ecat as a supplementary cementitious material (SCM).

Figure 4: Effect of phosphogypsum on the axial compressive strength of cement mixtures at 48 hours of hydration (25°C)



3.2 PERFORMANCE OF COMPOSITE CEMENTS CONTAINING ECAT AS A SUPPLEMENTARY CEMENTITIOUS MATERIAL AND PHOSPHOGYPSUM AS A SET CONTROLLER

The influence of two different types of phosphogypsum (SP and MG) and Ecat on the heat of hydration of cement pastes is shown in Figure 5. In all samples, it is possible to identify the five main stages found in hydrated cements: initial reaction, induction period, acceleration period, deceleration period, and slow reaction period [32]. The onset of the acceleration period leads to the main C_3S hydration reaction, characterized by a period in which the reaction accelerates to a peak, followed by a deceleration period [17]. At this stage, the reaction rate decreases progressively as the availability of reactive phases in the system decreases [16].

The higher heat flux observed in the CPII-Z formulations and in the reference sample containing analytical-grade calcium sulfate, without Ecat addition (SE-REF), indicates more pronounced hydration kinetics during the first few hours. A longer induction period is observed in the CPIV formulations, both those composed of phosphogypsum and those with analytical-grade calcium sulfate, indicating a delay in the initial hydration reaction. This behavior may be associated with the high Ecat content, which alters the sulfate-to-aluminate ratio in the system. In these samples, this stage begins only after approximately 5 hours of hydration and exhibits a lower heat flux, indicating a slower initial reaction rate. However, the CPII-Z and SE-REF formulations exhibit a shorter induction period, with acceleration beginning at around 2.5 hours and 1 hour, respectively. From a technological standpoint, the induction (or dormant) period is critical, as it corresponds to the interval during which the concrete remains workable, allowing for its transport and placement before hardening begins [17]. In the CPII-Z-SP4, CPII-Z-MG4, CPII-Z-REF, and SE-REF samples, the C_3S and aluminate reaction peaks overlap, which may have occurred due to a sulfate deficiency in these systems [32]. However, for the CPIV-REF, CPIV-MG4, and CPIV-SP4 samples, a secondary peak is identified in the heat flow curves, associated with sulfate depletion [21] and the hydration of the remaining aluminates and C_3A, with the consequent formation of AFm phases [5]. The occurrence of this shoulder in the CPIV formulations is explained by the higher Ecat content in these systems, which implies a lower clinker content and greater availability of aluminates and, consequently, a higher fraction of remaining aluminates after the initial consumption of sulfates, resulting in the formation of monosulfoaluminates.

Figure 5: Heat flow of composite cement mixtures over 144 hours of hydration (25°C)

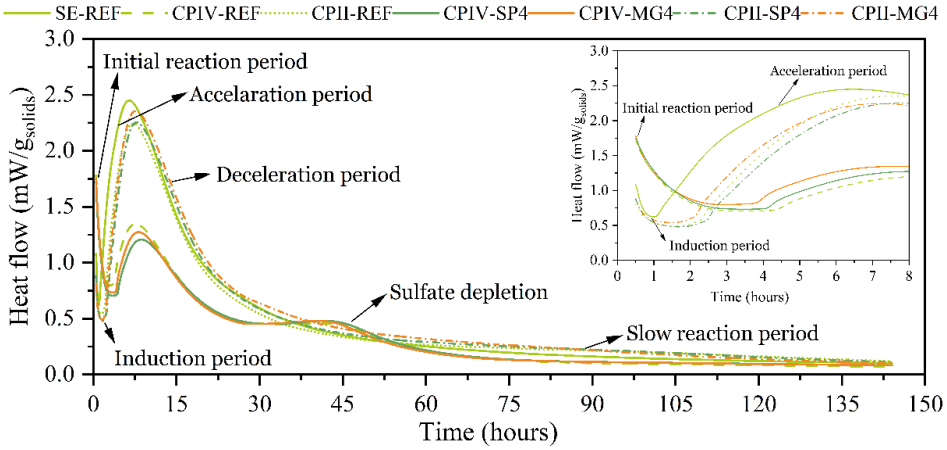
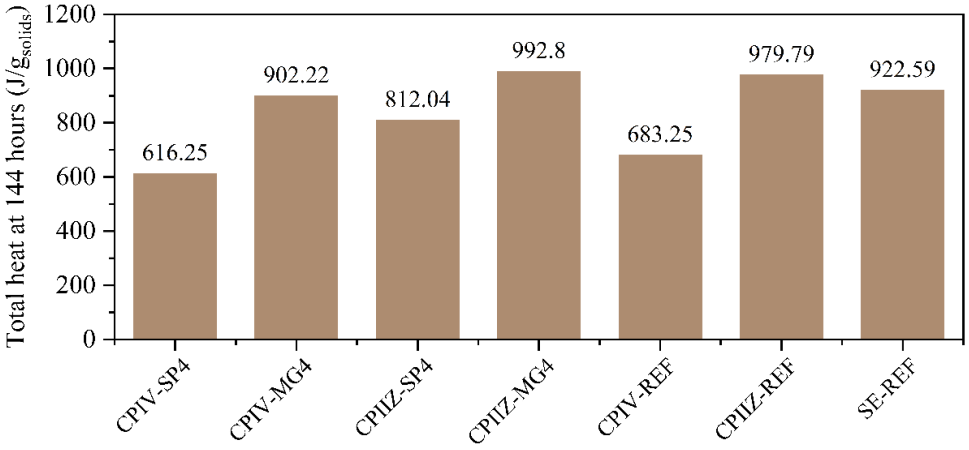


Figure 6 shows the heat accumulated over 144 hours, allowing for an evaluation of the combined effect of phosphogypsum and Ecat on the hydration kinetics.

Figure 6: Total heat of the mixtures after 144 hours of hydration (25°C)

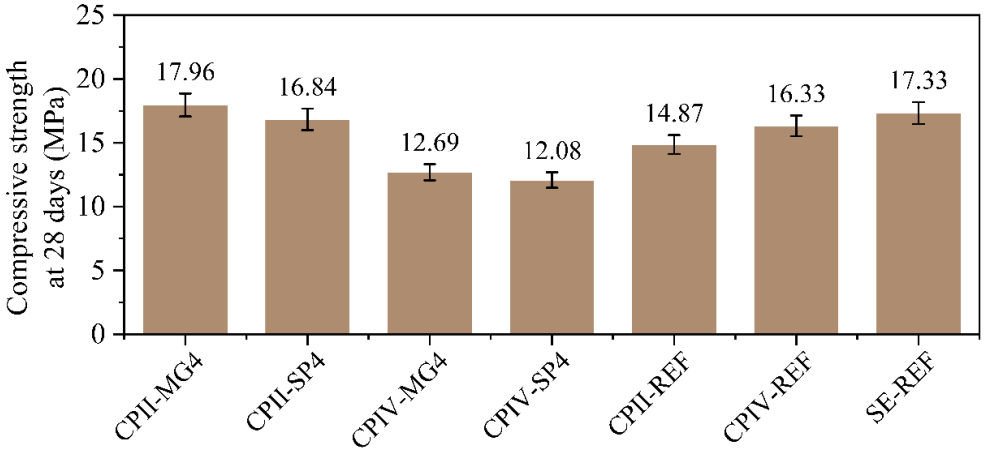


For the CPIV systems, the CPIV-MG4 and CPIV-SP4 formulations have identical compositions in terms of clinker content (46%), Ecat (50%), and phosphogypsum (4%), differing only in the source of the phosphogypsum. As expected, all CPIV formulations, characterized by a lower clinker content, exhibited lower accumulated heat when compared to the equivalent CPII-Z formulations. Among the CPIV cements, it is observed that the CPIV-MG4 sample (902.22 J/g$_{solids}$) exhibits a higher total accumulated heat compared to CPIV-SP4 (616.25 J/g$_{solids}$), indicating a higher degree of hydration at the end of the evaluation period. This behavior suggests that phosphate gypsum from Minas Gerais exhibits chemical characteristics that favor reaction kinetics, promoting greater sulfate solubility [6]. A similar trend was observed for the CPIIZ-MG4 (992.80 J/g$_{solids}$) and CPIIZ-SP4 (812.04 J/g$_{solids}$) systems, which also have equivalent clinker contents (82%), Ecat (14%), and phosphogypsum (4%), reinforcing that the differences observed in the accumulated heat are associated with the type of phosphogypsum used (Figure 6).

The comparison with the reference samples, formulated with analytical-grade calcium sulfate, allows for isolating the influence of Ecat on the hydration kinetics (Figure 6). It is observed that CPIIZ-REF exhibits accumulated heat close to that of SE-REF (without Ecat), indicating that, at moderate levels, Ecat does not compromise the hydration reactions. However, CPIV-REF shows a significant reduction in the total heat released, demonstrating that, at high levels, Ecat alters the sulfate/aluminate equilibrium of the system. It has been found that trace elements present in the catalyst can affect phase dissolution and influence the kinetics of hydration [33]. Furthermore, the catalyst influences the heat of cement hydration, with even small added quantities accelerating the kinetics of the process [34].

Figure 7 shows the axial compressive strength results for the composite cement pastes at 28 days of hydration. As expected, the pastes with a higher clinker content and thus a higher C_3S content exhibited higher compressive strength compared to the CPIV pastes. The CPIIZ-MG4 (17.96 MPa) and CPIIZ-SP4 (16.84 MPa) formulations exhibit the highest values among the systems with added phosphogypsum, surpassing CPII-REF (14.87 MPa), which suggests that, at moderate levels of substitution, the system maintains satisfactory mechanical performance.

Figure 7: Axial compressive strength of composite cement pastes at 28 days (w/c = 0.50)



The difference between MG4 and SP4 is slight, indicating that, for the CPII-Z system, the source of the phosphogypsum does not have a decisive influence on the final strength. In the CPIV system, a different behavior is observed. The CPIV-REF (16.33 MPa) exhibits intermediate strength, lower than that of CPIIZ-MG4 and SE-REF (17.33 MPa), but higher than that of CPIV formulations containing phosphogypsum. The CPIV-SP4 (12.08 MPa) and CPIV-MG4 (12.69 MPa) samples exhibit a significant reduction in strength, demonstrating that, in systems with high clinker replacement (50% Ecat), mechanical performance becomes more sensitive to chemical equilibrium and hydration kinetics, possibly due to the reaction between the aluminates and the sulfates in the PG [35]. The SE-REF sample (17.33 MPa) confirms the trend toward higher strength in systems with greater availability of clinker phases.

In general, the results indicate that, in the CPIV system, there is a reduction in the mechanical strength of the pastes, regardless of the origin of the phosphogypsum. This behavior may be associated with alterations in the sulfate-aluminate equilibrium and hydration kinetics, since the availability of sulfate can influence the formation of hydrated phases containing aluminate and the development of mechanical strength in cementitious systems with mineral additions [36]. On the other hand, in the CPII-Z compositions, a distinct behavior is observed, with improved strength, which can be attributed to the lower Ecat content and the greater proportion of clinker in the system. In these formulations, clinker reactions, in the presence of phosphogypsum, become predominant, favoring hydration products and contributing to better structural performance. Similar behavior was reported by [10], who observed a reduction in compressive strength with increasing Ecat content relative to the reference cement paste (w/c = 0.5). A joint analysis of the mechanical strength and calorimetry results indicates that the higher heat released in the CPIV-MG formulation did not translate into increased strength. This behavior suggests that part of the exothermic reactions is associated with the interaction of aluminates with species present in the phosphogypsum and does not contribute significantly to the formation of products responsible for the mechanical enhancement.

Figure 8 shows the diffractograms of the composite cement pastes analysed. The crystalline phases identified include alite, belite, ettringite, calcium hydroxide (portlandite), and calcite. It can be inferred that C-S-H gel forms as a hydration product in composite cement matrices; however, due to its predominantly amorphous nature, this phase does not exhibit defined diffraction peaks in the diffractograms [37]. The presence of C_2S and C_3S is attributable to non-hydrated or residual clinker. The peaks of highest intensity are associated with ettringite and portlandite, indicating that these phases

constitute the main hydration products formed during the reactions in the analysed pastes. Ettringite crystals can accelerate the hydration of the C-S-H phases and increase compressive strength [13]. Small amounts of $CaSO_4 \cdot 2H_2O$ are present, most evident in the CPIV-type formulations (Table 2).

Figure 8: XRD of composite cement pastes at 28 days (w/c = 0.5)

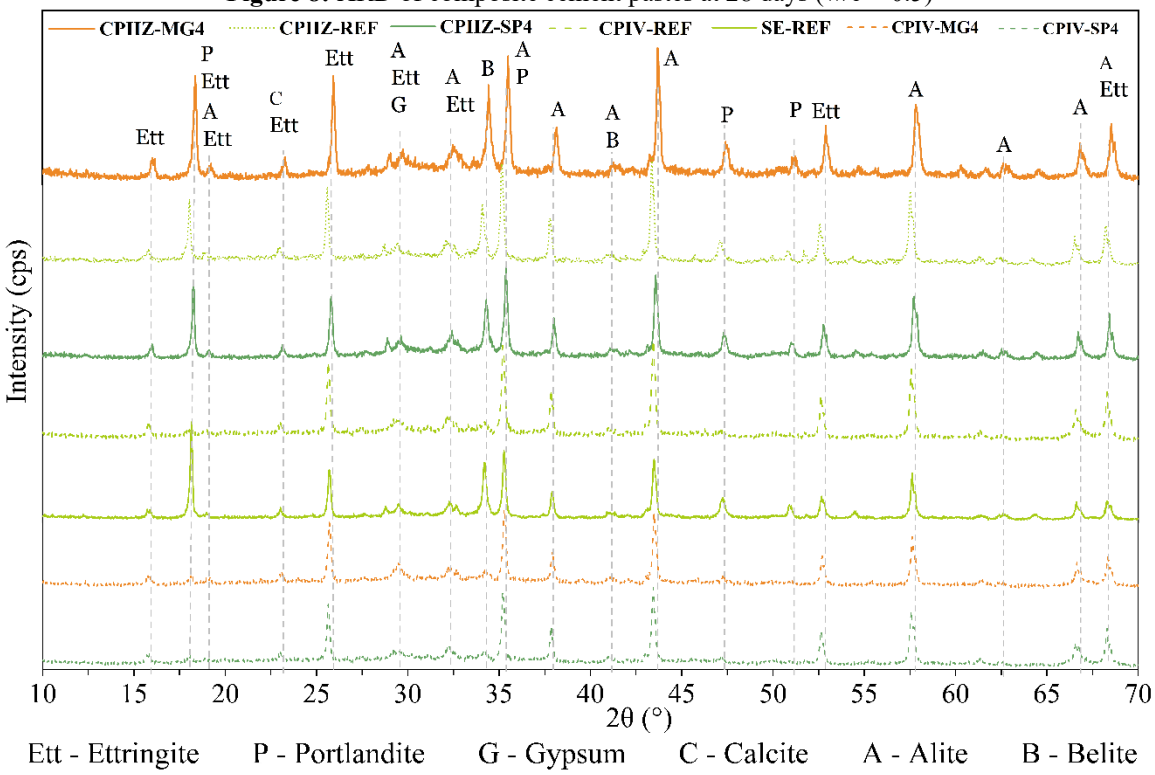


Table 2: Mineralogical composition of composite cement pastes at 28 days

Phase (%)	Composition (%)	CPII-REF	CPIV-REF	SE-REF	CPII-MG4	CPII-SP4	CPIV-MG4	CPIV-SP4	ICSD code
Calcite	$CaCO_3$	0.89	1.95	1.86	1.35	1.49	3.98	1.73	79673
Gypsite	$CaSO_4.2H_2O$	0.65	1.29	0.31	0.40	0.31	0.98	1.02	151692
Ettringite	$Ca_6Al_2(OH)_{12}(SO4)_3 \cdot 26H_2O$	7.04	9.14	6.73	8.74	8.43	10.21	9.71	155395
Portlandite	$Ca(OH)_2$	8.39	2.77	13.98	11.05	10.88	2.32	1.82	15471
Belite (C_2S β)	$2CaO.SiO_2$	4.95	4.49	5.42	4.65	5.42	4.58	5.28	79550
Alite (C_3S M3)	$3CaO.SiO_2$	5.93	5.68	3.51	4.31	3.46	4.47	5.08	94742
Amorphous and unidentified crystalline phase (ACn)	-	72.14	74.68	68.19	69.87	70.01	73.46	75.36	-
Rwp	-	14.99	14.02	17.39	17.58	15.34	12.85	12.46	-
GOF	-	1.57	1.47	1.68	1.41	1.36	1.30	1.32	-

As described by [37], the intensity of the peak corresponding to gypsum tends to decrease as hydration progresses, particularly at 28 days. It is observed that the CPIV formulations have higher ettringite contents (9.14-10.21%) and lower portlandite contents (1.82-2.77%) compared to the CPII-Z formulations and the SE-REF sample, which exhibit greater formation of $Ca(OH)_2$ (up to 13.98%). This behavior indicates that, in systems with high Ecat content, there is greater consumption of calcium hydroxide, possibly associated with the pozzolanic reaction of the catalyst's amorphous aluminosilicates, corroborated by the higher content of amorphous material (73-75%) in these formulations (Table 2). This consumption of portlandite and the higher availability of aluminates favor the prolonged formation of ettringite, which explains the second peak observed in the calorimetry of the CPIV samples.

The significant reduction in $Ca(OH)_2$ indicates intense consumption of this compound due to the pozzolanic reactions of Ecat. Similar results were observed in a previous study [8]. In the samples containing composites with partial replacement of cement by the residual catalyst, there was a consumption of calcium hydroxide compared to the reference sample. The SE-REF sample (17.33 MPa), which had the highest portlandite content (13.98%) and lowest amorphous fraction (68.19%), shows hydration dominated by the primary reactions of the clinker, with more intense formation of C-S-H, resulting in higher strength (Figure 8).

4 CONCLUSION

The results demonstrate that phosphogypsum is a viable alternative sulfate source for Portland cement systems, provided that its content is adjusted to ensure an appropriate balance between hydration kinetics and mechanical performance. Among the proportions evaluated, 4% phosphogypsum provided the most favorable performance, whereas higher contents compromised compressive strength. The origin of phosphogypsum also influenced hydration behavior, highlighting the importance of its characteristics in cement formulation.

The incorporation of Ecat affected the performance of the composite cements depending on the replacement level. In CPII-Z formulations, phosphogypsum combined with 14% Ecat improved compressive strength compared with the corresponding reference system. Conversely, CPIV formulations containing 50% Ecat exhibited reduced mechanical performance, despite greater portlandite consumption and ettringite formation, indicating that enhanced hydration reactions do not necessarily translate into higher strength.

Overall, the findings support the combined use of phosphogypsum and Ecat in composite cement formulations, particularly at moderate clinker replacement levels. However, their effective incorporation requires optimization of sulfate availability and Ecat content to achieve a suitable balance between hydration behavior and mechanical performance

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Author Contributions: R. S. P.: Conceptualization, Methodology, Data Curation, Formal Analysis, Writing-original draft preparation, review and editing. **S. R. C.:** Conceptualization, Methodology, Data Curation, Formal Analysis. **B. S. R.:** Formal Analysis. **L. B. B. B.:** Data Curation. **J. P. G.:** Conceptualization, Supervision.