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Insights into the effect of the sulfate-to-alkali ratio on the C_3A polymorphism of lab-synthesized Portland clinkers.

Insights no efeito da relação sulfato/álcali no polimorfismo do C_3A em clínqueres Portland sintetizados em laboratório

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Abstract
This study investigates the effects of sulfate-to-alkali ratio and alkali type on C_3A polymorphism in laboratory-synthesized Portland clinkers. Clinkers were produced using controlled raw meal compositions with external doping of sulfates and alkalis (Na_2O and K_2O). X-ray diffraction combined with Rietveld quantitative phase analysis (RQPA) was employed to determine phase assemblage and C_3A polymorphs distribution. Results show that increasing the sulfate-to-alkali ratio favors the stabilization of cubic C_3A in a moderate correlation strength (R^2 = 0.7273). However, significant differences were observed depending on alkali type. Sodium strongly promoted orthorhombic C_3A formation, reaching up to 45 wt.% of this polymorph, whereas potassium showed a much weaker effect, even at similar sulfate-to-alkali ratios, generating only ~14 wt.% of this polymorph. These findings indicate that alkali type plays a more decisive role than the sulfate/alkali ratio alone when external alkali incorporation is considered. The results provide new insights into clinker phase formation under varying chemical conditions, highlighting the importance of distinguishing between Na and K effects, and for the laboratory synthesis environment.

Keywords: Portland clinker. C_3A. Polymorphism. Alkali. Sulfate-to-alkali ratio.

Resumo

Este estudo investiga os efeitos da relação sulfato/álcali e do tipo de álcali no polimorfimo do C_3A em clínqueres Portland sintetizados em laboratório. Os clínqueres foram produzidos a partir de composições controladas, com adição externa de sulfatos e álcalis (Na_2O e K_2O). A difração de raios X, combinada com a análise quantitativa de fases pelo método de Rietveld (RQPA), foi empregada para quantificar a formação de fases e a distribuição dos polimorfos de C_3A. Os resultados mostram que o aumento da relação sulfato/álcali favorece a estabilização do C_3A cúbico em uma correlação moderada (R^2 = 0.7273). No entanto, diferenças significativas foram observadas em função do tipo de álcali. O sódio promoveu fortemente a formação de C_3A ortorrômbico, resultando em 45 wt.% desse polimorfo, enquanto o potássio apresentou um efeito muito mais limitado, mesmo para relações sulfato/álcali semelhantes, apresentando apenas aproximadamente 14 wt.% desse polimorfo em relação ao total de C_3A. Os resultados obtidos indicam que o tipo de álcali desempenha um papel mais decisivo do que a relação sulfato/álcali isoladamente quando há incorporação externa de álcalis.

Palavras-chave: Clínquer Portland. C_3A. Polimorfismo. Álcali. Relação sulfato/álcali.

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INTRODUCTION

Considering the goal of achieving net-zero CO_2 emissions by 2050, the cement industry is increasingly adopting strategies to enhance its overall sustainability [1,2]. The use of supplementary cementitious materials (SCMs) to reduce the clinker factor [3,4] plays a central role in this transition. In addition, the development of alternative low-carbon binders [5,6] and the implementation of carbon capture, utilization, and storage (CCUS) technologies [7] are widely recognized as key pathways toward decarbonization. Alongside these approaches, the adoption of alternative raw materials and fuels in clinker production, a process also known as co-processing—has gained significant attention and is being progressively implemented in industrial practice [8,9].

Co-processing reduces the reliance on conventional carbon-intensive fuels by incorporating alternative fuels and raw materials into the production process [9]. However, despite its environmental advantages, this approach introduces additional variables into clinker synthesis [10,11], often leading to variations in clinker chemistry and structure. These changes are particularly relevant to phase formation, polymorphic distribution, and, consequently, the hydration behavior of the resulting cementitious systems [9, 11-13].

Alkalis and sulfates are commonly introduced into the kiln through these fuels and raw materials, and their effects are not always fully accounted for during clinker production. These elements are closely associated with changes in C_3A formation [11,14] and can combine to form alkali sulfate phases [13]. However, when the alkali content exceeds the available sulfate required for full alkali incorporation into these alkali sulfates, the excess alkalis can interact with the C_3A phase, influencing its polymorph stabilization [15]. At higher alkali contents, the orthorhombic C_3A polymorph is typically stabilized, whereas low-alkali clinkers tend to favor the cubic form [13,16]. The monoclinic polymorph is rarely observed in commercial Portland cements [13,16].

Despite the established link between alkali content and C_3A polymorphism, the sulfate-to-alkali ratio is recognized as a key controlling parameter for these variations [13]. Accordingly, the presence of alkalis alone may not be decisive if sufficient sulfate is available to incorporate them into alkali sulfate phases. In contrast, the specific role of alkali type (i.e., sodium versus potassium) remains poorly understood, as most studies treat alkalis as a single combined parameter without distinguishing between these elements.

In this context, the present study aims to investigate the combined effects of the sulfate-to-alkali ratio and alkali type on C_3A polymorphism in laboratory-synthesized Portland clinkers. Controlled compositions and raw materials were employed to explore a wide range of formulations, providing new insights into this complex and still not fully understood topic. The central hypothesis of this study is that Na and K may exert distinct influences on C_3A polymorph stabilization, and that the nature of the alkali ion is a decisive factor governing the orthorhombic-to-cubic C_3A transition in Portland clinker systems, along with the also discussed sulfate-to-alkali ratio.

EXPERIMENTAL PROGRAM

RAW MATERIALS

In this study, an industrial raw meal supplied by a Brazilian cement industry was used as the basis for clinker synthesis. The material exhibited a lime saturation factor (LSF) of 103.78, a silica modulus (SM) of 2.75, and an alumina modulus (AM) of 1.68. Its chemical composition, determined by X-ray fluorescence (XRF) using a Zetium (PANalytical) instrument, is presented in Table 1.

Table 1: Chemical composition of the raw meal used as the basis for the clinker production.

Oxide	Content (wt.%)
SiO_2	13.44
Al_2O_3	3.06
Fe_2O_3	1.82
CaO	44.03
SO_3	0.04
MgO	1.63
Na_2O	0.12
K_2O	0.65
Loss on ignition (950°C)	34.84

Source: Author (2026).

For the final synthesis, the industrial raw meal was adjusted to achieve target LSF, SM, and AM values consistent with laboratory conditions (i.e., without fuel ash contribution). This definition was based on previously reported parameters for Portland clinkers [10,13]. It is important to note that LSF values in industrial clinkers are naturally higher than those typically adopted in laboratory synthesis, since additional silica is commonly introduced into the kiln during fuel combustion, such as rice husk ash, effectively reducing the LSF of the final clinker. As this additional silica source is absent in laboratory synthesis, the LSF adopted here was intentionally set slightly below typical industrial values (which commonly range between 97 and 100), to reflect the expected composition of the laboratory-synthesized clinker rather than the industrial raw meal prior to burning.

Analytical-grade silicon dioxide (SiO_2, 98% purity), iron oxide (Fe_2O_3, 97% purity), and aluminium oxide (Al_2O_3, 99% purity) reagents were used for this purpose. In addition, doped clinkers were prepared by incorporating natural gypsum (45.07% SO_3 and 33.38% CaO) as a sulfate source, and sodium carbonate (Na_2CO_3, 98% purity) and potassium carbonate (K_2CO_3, 98% purity) as alkali sources.

SAMPLE PREPARATION AND CLINKER SYNTHESIS

The proportions of the raw materials were adjusted using SiO_2, Al_2O_3, and Fe_2O_3 to obtain a reference raw meal with LSF = 94.64 and AM = 1.37. For these fixed parameters, the SM of all samples ranged from 2.43 to 2.49. Sulfate incorporation, provided via natural gypsum, was set at 0.5%, 1.0%, and 1.5% by mass of raw meal. Alkalis were introduced as Na_2O and K_2O to achieve total contents of 1.05% and 1.33% by mass of raw meal respectively. The difference in absolute alkali content between

the two compositions is explained by the fixed sulfate-to-alkali ratio adopted in this study ($/A = 0.80 for both alkali-doped samples). Since Na_2O and K_2O have different molar masses, maintaining the same sulfate-to-alkali ratio requires different weight percentages of each alkali oxide.

Alkali-doped samples were produced with a fixed sulfate content of 1.0% SO_3. These proportions were designed to produce clinkers with varying sulfate-to-alkali ratios (ranging from 0.06 to 2.50) and different alkali sources. Details of the compositions adopted are presented in Table 2. The proportions adopted in this study were based on a wide study conducted by Andrade Neto et al. [13] and on previously conducted lab-synthesis of Portland clinkers [10].

Table 2: Proportions used for the Portland clinker synthesis.

Sample	LSF	AM	SM	$/A*	SO_3 (wt.%)	Na_2O (wt.%)	K_2O (wt.%)
REF	94.64	1.37	2.43	0.06	0.04	0.13	0.63
S_0.50	94.64	1.37	2.45	0.80	0.50	0.13	0.62
S_1.00	94.64	1.37	2.47	1.61	1.00	0.12	0.62
S_1.50	94.64	1.37	2.49	2.50	1.50	0.12	0.61
N_1.05	94.64	1.37	2.47	0.80	1.00	1.05	0.61
K_1.33	94.64	1.37	2.47	0.80	1.00	0.12	1.33

*Sulfate-to-alkali ratio = $\frac{\frac{SO_3}{80.06}}{0.5.\frac{Na_2O}{61.98}+\frac{K_2O}{94.20}}$

The raw materials were ground and homogenized in a ball mill for 20 minutes using 35 alumina balls per 200 g of powder. Particle size distribution of the raw meals is presented in Table 3. After each grinding cycle, the mill was cleaned with natural sand for 7 minutes to minimize contamination from residual materials. The resulting raw meals were then compacted into disks (35 mm diameter) under a load of 100 kN using an HTP 40 (Herzog) automatic press.

Table 3: Particle size distribution parameters of the raw meals.

Sample	D_{10} (µm)	D_{50} (µm)	D_{90} (µm)	Average particle size (µm)
REF	1.06	4.93	25.09	9.47
S_0.50	1.08	5.06	25.14	9.50
S_1.00	1.06	5.10	25.17	9.54
S_1.50	1.07	5.11	25.31	9.57
N_1.05	1.09	5.34	25.56	9.79
K_1.33	1.10	5.36	25.48	9.72

Source: Author (2026).

The compacted disks were subsequently sintered in a high-temperature LF1600 furnace (JUNG) to produce the clinkers. The clinkerization was carried out at a heating rate of 10 °C/min up to 1400 °C, followed by a 2-hour dwell at the maximum temperature. After sintering, the samples were rapidly cooled by forced air quenching using a fan to enhance clinker quality.

TEST METHODS

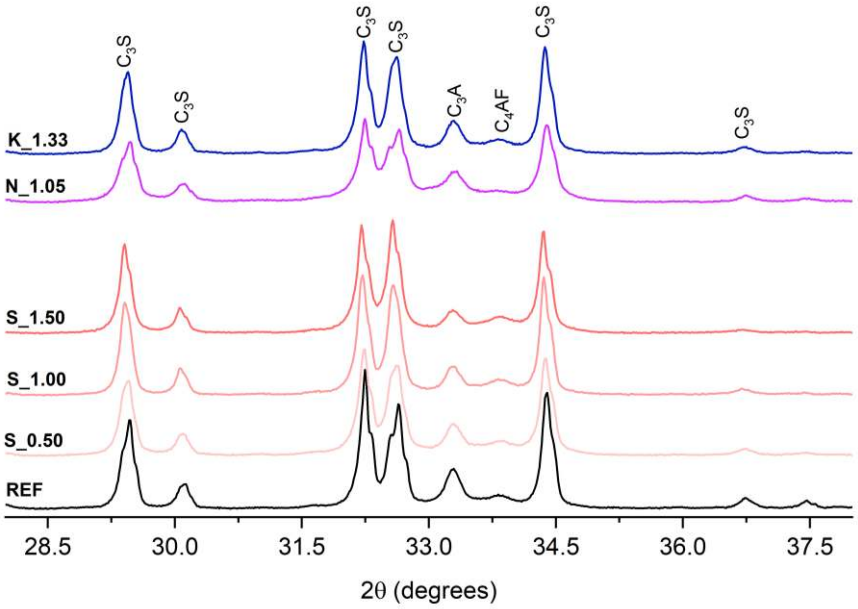
The laboratory-synthesized clinkers were characterized by X-ray diffraction (XRD) using an Empyrean (PANalytical) instrument operated at 45 kV and 40 mA with Cu Kα radiation. Data were collected over a 2θ range of 5–70° with a step size of 0.0131°/min. Phase quantification was performed through Rietveld quantitative phase analysis (RQPA) using TOPAS v7 software with crystallographic structural models retrieved from the Inorganic Crystal Structure Database (ICSD). Background was modeled by a fourth-order Chebyshev polynomial, and lattice parameters were refined for all identified phases. No internal or external standard was employed, as the amorphous content of the synthesized clinkers was considered negligible. Portland clinker is composed almost entirely of well-crystallized phases, and the controlled laboratory synthesis conditions further favor complete crystallization, making amorphous phase quantification unnecessary for the purposes of this study.

The RQPA enabled quantification of all crystalline phases, with particular emphasis on the identification and quantification of C_3A polymorphs. This approach provided further insight into the direct influence of the sulfate-to-alkali ratio on the formation and stabilization of aluminate phases in the synthesized clinkers.

RESULTS AND DISCUSSION

Figure 1 presents the XRD patterns of laboratory-synthesized clinkers with varying sulfate and alkali contents, while Table 3 summarizes the corresponding RQPA results. The diffractograms confirm the formation of the main Portland clinker phases (i.e., C_3S, C_3A, and C_4AF), indicating successful clinkerization. No significant diffraction peaks associated with free lime were observed, suggesting its absence or presence only in minor amounts. This observation is further supported by the quantitative phase analysis, which shows low free lime contents ranging from 0.45% to 1.05% across all samples. These results collectively confirm the high quality of the synthesis and the effectiveness of the clinkerization process.

Figure 1 – XRD patterns of the synthesized clinkers. Crystallographic models used for phase identification: C_3S (ICSD 94742), C_4AF (ICSD 52783), and C_3A (ICSD 1841).



Source: Author (2026).

Table 3: Phase distribution of the synthesized clinkers obtained through RQPA.

Phase	REF	S_0.50	S_1.00	S_1.50	N_1.05	K_1.33
M1-C_3S	33.74	33.98	41.70	40.92	23.64	34.65
M3-C_3S	43.12	44.28	38.01	39.86	51.93	43.50
Total C_3S	76.86	78.26	79.71	80.78	75.57	78.15
C_2S	4.92	4.90	4.90	4.27	6.05	4.78
Cubic C_3A	8.40	7.61	6.59	5.47	5.11	7.90
Orthorhombic C_3A	2.17	1.36	1.08	0.80	5.45	1.22
Total C_3A	10.57	8.97	7.67	6.27	10.56	9.12
C_4AF	5.63	6.32	6.34	7.28	5.69	6.24
Periclase	0.94	0.85	0.80	0.70	0.94	0.82
Free lime	1.05	0.65	0.45	0.55	1.03	0.575
Aphthitalite	0.03	0.03	0.06	0.05	0.00	0.29
Arcanite	0.00	0.00	0.06	0.08	0.15	0.01
Rwp	5.69	5.15	5,31	5,56	5,38	5,54

Source: Author (2026).

Considering the overall C_3A formation, clear differences in C_3A polymorphism can be identified, which constitute the main focus of this study. The ratio between orthorhombic and cubic C_3A was evaluated as a function of the sulfate-to-alkali ratio, and the results are presented in Figure 2.

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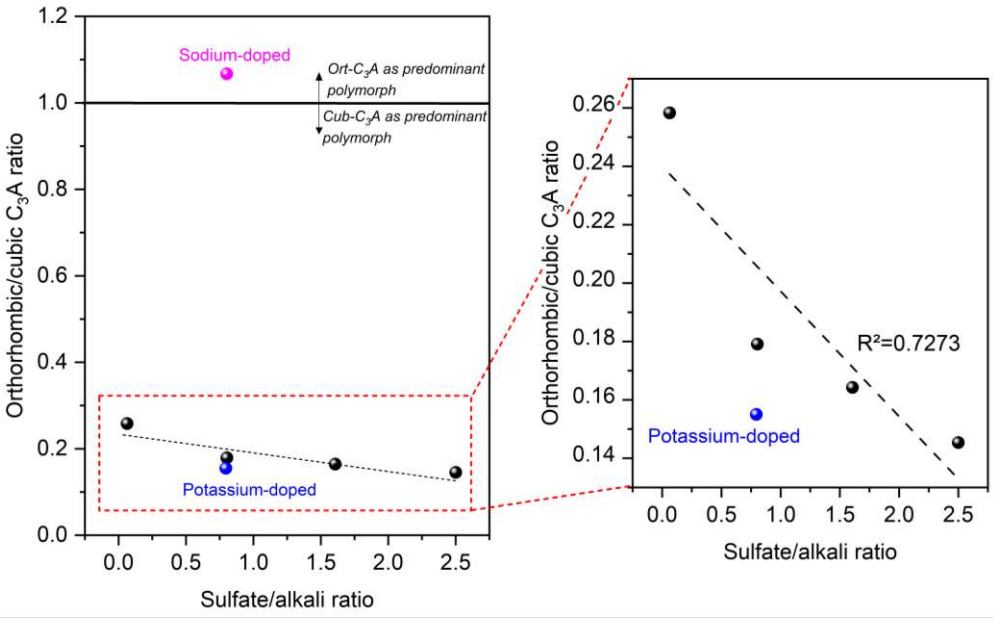
Figure 2: C_3A polymorphism distribution for different sulfate-to-alkali ratios across the synthesized clinkers.



Source: Author (2026).

An overall trend was identified in which the cubic C_3A polymorph predominates in most samples, with the exception of the sodium-doped clinker (N_1.05). A decrease in the orthorhombic-to-cubic C_3A ratio was observed with increasing sulfate-to-alkali ratio, indicating that higher sulfate/alkali ratios favor the formation of cubic C_3A at the expense of the orthorhombic form. A reasonable correlation was obtained for the REF, S_0.50, S_1.0, S_1.5, and K_1.33 samples (R^2 = 0.7273), in agreement with recent studies [13,17], reporting that higher sulfate-to-alkali ratios promote the stabilization of cubic C_3A.

However, a clear outlier is observed for the sodium-doped clinker (N_1.05), which deviates significantly from the established correlation and exhibits a markedly distinct C_3A polymorph distribution. This behavior suggests that Na^+ and K^+ exert fundamentally different influences on C_3A polymorphism. While the K-doped clinker (K_1.33) followed the same trend as the sulfate-doped series, with cubic C_3A remaining dominant, the N_1.05 clinker was the only composition in which the orthorhombic polymorph prevailed. This divergence indicates that the nature of the alkali ion, rather than the alkali content or the sulfate-to-alkali ratio alone, plays a decisive role in determining C_3A polymorphism. While the effects of Na_2O and K_2O are often treated as equivalent in the literature [15], the present results clearly challenge this assumption, demonstrating that these two alkalis interact differently with the C_3A crystal structure and should not be considered interchangeable when assessing their influence on clinker mineralogy.

To further investigate the effect of alkali type, three samples with the same sulfate-to-alkali ratio (fixed at 0.80) were compared, as shown in Figure 3. The S_0.50 sample (black dot) contained only 0.50% SO_3, while the K_1.33 (1.33% K_2O) and N_1.05 (1.05% Na_2O) samples were doped with external alkalis and 1.0% SO_3. Although these compositions yield the same sulfate-to-alkali ratio, they result in markedly different C_3A polymorph distributions.

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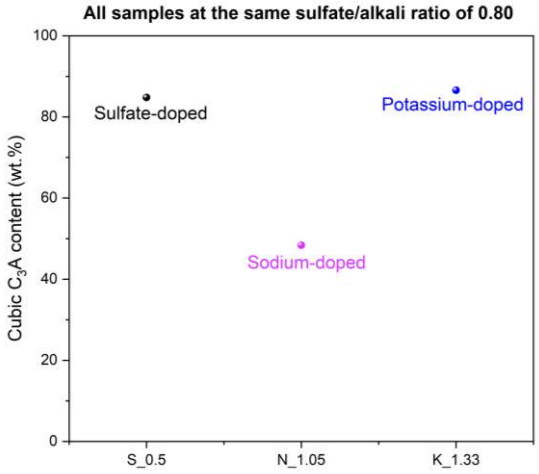
Figure 3: C_3A polymorphism distribution for different alkali presence and type for the same sulfate-alkali ratio of 0.80.



Source: Author (2026).

The S_0.50 and K_1.33 samples exhibited very similar behavior, with cubic C_3A representing 83.4% and 84.6% of total C_3A, respectively, confirming the predominance of the cubic polymorph in these systems. In contrast, the sodium-doped sample (N_1.05) showed a significantly different response, with only 48% cubic C_3A, making it the only sample in which the orthorhombic polymorph predominates.

These results highlight that alkali type and incorporation play a more decisive role in C_3A polymorphism than the sulfate-to-alkali ratio alone. While, in the absence of external alkali addition, increasing the sulfate-to-alkali ratio favors cubic C_3A stabilization, the presence of Na_2O strongly promotes the formation of orthorhombic C_3A. In contrast, K_2O appears to have a much weaker influence on this polymorphic transition.

CONCLUSIONS

This study presented the laboratory synthesis of Portland clinkers with varying sulfate-to-alkali ratios, achieved through controlled external doping of sulfates and alkalis, in order to investigate their specific effects on C_3A polymorphism stabilization.

The differences observed may be hypothesized to arise from the distinct sintering conditions in a laboratory stationary furnace, where potassium may not be incorporated into the C_3A structure to the same extent as sodium. From an industrial perspective, however, sodium and potassium are typically present simultaneously, and their combined effect is often interpreted as a general “alkali effect” on C_3A polymorphism. The present results suggest that this assumption may oversimplify the phenomenon, as Na_2O appears to play a more dominant role in stabilizing the orthorhombic C_3A polymorph, while K_2O exerts a comparatively weaker influence.

These findings highlight the need to distinguish between alkali types when assessing their impact on clinker phase development. The differences identified here between alkali type effects and sulfate-to-alkali ratio contributions provide a valuable basis for future investigations into the complex mechanisms governing aluminate phase formation and polymorphism in Portland clinker.

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DECLARATIONS

During the preparation of this manuscript, the first author used Claude (Sonnet 4.6, Anthropic) as an AI-assisted writing tool to support grammar revision and text clarity improvement. The authors subsequently reviewed and edited all AI-assisted content and take full responsibility for the integrity and accuracy of the published work.

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