

RESEARCH ARTICLE

Microstructure and hydration of interstitial in clinkers produced over molten steel

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Abstract

Scalable electrical production of clinker is possible under reducing conditions, and the reactivity of C_3A produced in such conditions has only been superficially described. We examined electric clinkers made over molten steel with a range of fineness and compared them against commercial clinkers. Using x-ray diffraction, calorimetry, and backscattered electron microscopy/image analysis, we investigated the roles of morphology, crystal structure, and phase interaction. Shortage of Fe^{3+} ions in the interstitial in electric clinkers makes its C_3A more reactive like white cements and synthetic systems. In the presence of ferric oxides, ferrite is formed and the concentration of dissolved Fe^{3+} ions in C_3A increases. The kinetics of C_3A hydration are hindered both by the ferrite phases intermixing with the C_3A phase, hence acting as a physical barrier for dissolution, and by Fe^{3+} ions dissolving in C_3A , thereby reducing its intrinsic reactivity. Although this higher reactivity of C_3A requires more gypsum to ensure proper sulfation, this can be managed by controlling fineness and blending with supplementary cementitious materials.

KEYWORDS

clinker production, electric arc furnace, electric cement, Portland cement, reducing condition, tricalcium aluminate

1 | INTRODUCTION

Portland cement clinker production has transformed significantly over the last two centuries.^{1,2} A 2025 state-of-the-art cement plant uses less than one-fifth of the energy needed by the early cement plants in the nineteenth century. Products made from cement have also become 10 times stronger (based on 28 days strength tests). Finally, the production capacity of cement plants has increased thousands of times.^{1,3–5} Annually, cement clinker production is responsible for ~2.4 billion tonnes of CO_2 emissions

globally.⁶ These arise from both limestone decomposition and fuel combustion. Over time, the use of limestone has increased marginally to produce cements with higher alite content. Most cement plants today aim to reduce their use of coal and petroleum coke by partial substitution with natural gas and alternative fuels⁷ such as waste-derived fuels or biomass. Alternative fuels do not eliminate CO_2 emissions, and there is limited availability of biomass.^{8–10} Energy efficiency has also reached a plateau with the adoption of preheaters and multi-stage cyclone pre-calciners in modern cement plants. Any

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further emissions reduction depends on a technological breakthrough.¹¹

Most cement producers have pledged to produce clinker with net zero emissions by 2050. Fuel combustion emissions could be eliminated by process electrification, but this would have no effect on the emissions linked to process chemistry. The industry's plans are therefore largely based on the deployment of carbon capture and storage at existing cement plants.^{12,13} Although carbon capture is technically possible, the flue gases from cement plants are mostly N_2 and typically have only 12%–20% CO_2 , so separation of a pure stream of CO_2 is energy intensive and costly. Meanwhile, global capacity for storage today is negligible.

To eliminate emissions from clinker production, a decarbonated source of calcium must be used as a feedstock. The use of a decarbonated source of calcium has the additional benefit of energy savings, as most of the energy used to produce cement clinker is for the calcination of limestone as much of the energy required for heating can be recovered from coolers.¹⁴ The level at which limestone can be replaced as a raw material depends on the lime ratio of the decarbonated calcium sources with respect to silica, alumina, iron oxides, and the amount of MgO. Recovered cement pastes (RCPs) from construction demolition wastes are a potential source of decarbonated calcium.^{15,16} The major hurdle to its use is the requirement for good quality separation of the cement paste from the silica-rich aggregate. Today, there are new promising processing routes to increase the lime content in the RCP and produce better quality recovered aggregates.^{17–20} It should be noted that even with perfect separation, the presence of limestone added as a filler or carbonation of concrete could induce some CO_2 emission.

Further to decarbonating the feedstock, the electrification of heat in cement production is needed to reduce the emissions substantially depending on the grid. The decarbonation of the grid is an ongoing process.²¹ The emissions associated with combustion could be all but eliminated if the grid were powered by low-carbon sources. There are efforts aiming to reduce the fuel used for combustion by partially supplying heat electrically, using a plasma torch,^{11,22,23} resistive heating,²⁴ microwave,^{25,26} gas heating by rotors,²⁷ and so on, or by using “green” hydrogen as a fuel.¹¹ None of them seem to be mature enough at present to be upscaled and would need substantial research before commercial application.

Electrical heat at temperatures over 1400°C is common in electric arc furnaces (EAF) used to produce conductive materials, primarily steel. However, clinker and its raw materials are insulating. Luckily, steel is a conductor, has a melting point above the clinkering temperature, and is chemically compatible with clinker. In the previous work, we have demonstrated that molten steel in an EAF could

provide the heat for clinkering.²⁸ However, steel must be kept in a reducing atmosphere, as oxidation would otherwise transform the metallic steel to a large pool of *iron ore*. In contrast, for two centuries, clinker has been made in fully oxidizing conditions to enable combustion of carbon and to ensure iron in the clinker is fully oxidized as ferric (Fe^{3+}) oxide.

Although not intentional, it is possible to have a reducing flame in the conventional clinker production process when the availability of oxygen is not sufficient or when there is oxidizable material in the feedstock. The reducing condition in the kiln is easily identified by the change in color in the clinker nodules.^{29–31} Clinkers produced in reducing conditions are predicted to be of inferior quality due to the decomposition of alite to belite and free lime.^{31,32} This might be a larger concern when the clinker is not adequately cooled.²⁹ When clinker is produced in a reducing condition, iron reduces from Fe^{3+} to Fe^{2+} or metallic $Fe(0)$, and as a result, the calcium-alumino-ferrite phase (C_4AF , more general form: $C_{2(1+x)}A_xF_{2-x}$, where x varies from 0 to 1 [cement chemistry notation— $CaO:C$; $SiO_2:S$; $Al_2O_3:A$; $Fe_2O_3:F$; $H_2O:H$; $SO_3:\$$]) is expected to be lower or absent.

Our previous work,²⁸ demonstrating re-clinkering of cement paste over molten steel in reducing conditions, we found evidence of FeO formation and metallic iron from x-ray diffraction (XRD) measurements. Compared to the reference cement, which we re-clinkered, the alite content was higher (even up to 70% vs. 53% in reference cement) and ferrite content was lower (<2% vs. 10% in reference cement). The increase in alite content was attributed to the increase in lime saturation due to the presence of limestone and gypsum in commercial CEM I cement and possibly also due to the higher clinkering temperature (>1600 vs. ~1450°C in rotary kilns) and fast cooling in air due to small quantity (1–2 kg). The C_3A content was found to be around 2% higher in the electric clinkers compared to the reference cement. The gypsum requirement for proper sulfation (gypsums or calcium sulfates are added to cement to control the setting time and the optimum sulfate content is often described based on the calorimetry results, when C_3A hydration peak occurs after C_3S hydration peak) and the intensity of the calorimetry peak associated with C_3A hydration were also considerably higher than cement produced in a conventional process. It was not clear why C_3A hydrates differently in such systems.

When the overall alumina content is unchanged and it has lower ferrite content due to reducing conditions, the clinker so produced could have higher C_3A content.³³ Locher²⁹ has reported, based on Sylla's work, that C_3A content will increase in a reducing condition, particularly when cooled at a slower rate. They further reported faster setting of cements produced in a reducing condition and slow cooling rate and concluded that this is due to increase

in C_3A content and reactivity. The increase in C_3A content due to lack of ferrite could be as much as 3% compared to the cement produced in oxidizing condition. Such an increment of C_3A is not very significant, as in literature, a wide variety of Portland cements are reported with very different C_3A content, ranging from 4% to around 11%.^{34–37} In the isothermal calorimetry results presented in these papers, C_3A appears as a low-intensity peak near the main alite hydration peak, unlike the sharp intense peak in ref. 24 This leads to the conclusion that the pronounced peaks in the electric clinkers produced in reducing conditions are due to the higher reactivity of C_3A in such cements. This is of practical importance as proper sulfation is required to avoid loss of performance, both at early and late ages.

Our hypothesis was that the reactivity of C_3A is related to the availability of ferric oxides in the interstitial. As electric clinkers are produced in a highly reducing condition over molten steel, they have lower ferric oxides than typical Portland cement produced in a rotary kiln. We performed a detailed characterization and hydration study of electric clinkers with different fineness and compared them with commercial clinkers and cements. Two different commercial grey clinkers with different C_3A content (4% and 8% C_3A) were used to confirm the differences in reactivity were not caused by the higher C_3A content in electric clinkers. Two commercial cements (grey and white) were further used as controls. This study aims to explain the influence of C_3A formed under reducing conditions on the hydration of electric clinkers, without investigating the performance of the resulting cements.

2 | EXPERIMENTAL PROTOCOL

The microstructure and hydration of three electric clinkers produced over molten steel were investigated and compared against commercial clinkers and cements. A range of sulfate content was used to evaluate the sulfation behavior on clinkers, whereas sulfate content was not adjusted for commercial cements. The electric clinkers were produced by re-clinkering hydrated cement paste (HCP) in an induction furnace as described in our previous publication.²⁸ The three clinkers produced with the same feedstock were ground using different protocols to obtain clinkers of different fineness to further understand the effect of fineness that is known to have a significant impact on C_3A reactivity.

2.1 | Materials

HCP was used as a feedstock for production of electric clinkers over molten steel as it is an analogue of an RCP

from construction demolition waste that has had perfect separation. For the preparation of HCP, cement pastes were made by mixing commercial CEM I grey cement provided by Tarmac (Ref_PC_grey) with water and were transferred to plastic containers and were sealed (to prevent loss of moisture and avoid carbonation) and cured at ambient condition. To ensure high degrees of hydration, a relatively high water to cement ratio of 0.6 was used and was cured for 6 months. Afterward, they were removed from the containers and were heated at 500°C to remove the free and bound water in the cement paste and to replicate the process that is used to extract high-quality RCP.^{19,38} The loss on ignition (LOI) when fired to 900°C was found to be 13.8%. The normalized oxide composition of HCP after accounting for LOI will be same as Ref_PC_grey.

As controls, two commercial clinkers with varying C_3A content were used: Ref_Clinker_A8 and Ref_Clinker_A4, with 8% and 4% C_3A , respectively. The high C_3A clinker (Ref_Clinker_A8) was provided by Tarmac, and was from the same cement plant that produced the CEM I, which was used to produce HCP. The low C_3A clinker (Ref_Clinker_A4) was kindly provided by Katholieke Universiteit Leuven (KU Leuven) and was received as already ground. The commercial cement that was used to produce HCP was used as a third reference (Ref_PC_grey), and a white cement (Ref_PC_White) provided by Tarmac UK (Snowcrete, CEM I) was also used as an additional reference due to its lack of ferrite phases. The grey and white cements were received finely ground and blended with gypsum and limestone. For hydration studies, the ground clinkers were mixed with gypsum (VWR chemicals, AnalaR NORMAPUR).

2.2 | Production of electric clinkers

The electric clinkers were produced using an induction furnace in a graphite crucible. The leaching of carbon from the crucible ensured a highly reducing condition throughout. The feedstock for producing clinker was added along with the steel balls when the furnace was cold. Once the temperature was measured to be above 1600–1650°C, the clinker was tapped into a steel container using steel rods and was allowed to cool down under ambient air. Further details on the production could be found elsewhere.²⁸

To further grind the clinkers into powders, the clinkers were first crushed to a size less than 5 mm and the steel residues were removed using bar magnets. The clinkers were then ground to fine powder in a concrete mixer with 8 kg steel balls as charge. The steel balls had different sizes ranging from 5 to 40 mm. The mouth of the concrete mixer was covered with a plastic sheet to avoid

dust. The clinker was milled for 3 h at 16 rpm, and different feeds of 0.4, 1, and 1.5 kg were used to produce clinkers of varying fineness. Use of a smaller feed resulted in higher fineness. The clinkers thus produced were named Electric_6 μ , Electric_11 μ , and Electric_13 μ , indicating their median particle size. The un-milled commercial clinker (Ref_Clinker_A8) was also ground using the same protocol, excluding magnetic separation, using 1 kg of feed.

2.3 | Characterization methods

2.3.1 | X-ray fluorescence

The oxide composition of the clinkers was characterized at the Material Processing Institute at Middlesbrough, using wavelength dispersive x-ray fluorescence (WDXRF) spectroscopy. A Rigaku ZSX Primus IV x-ray fluorescence (XRF) spectrometer was used with the quantitative Fluxana raw calibration application. The samples were first heated in a muffle furnace at 900°C at a heating rate of 3°C/min and a holding time of 5 h. This ensured full oxidation of the samples before XRF analysis, and the loss or gain in ignition was noted down. The samples were then made into fused beads using lithium borate with a sample-to-flux ratio of 1:10.

2.3.2 | Particle fineness

The particle size distribution was measured by Meritics Ltd, using a Beckman Coulter particle size analyzer after the samples were dispersed in isopropanol. To analyze the raw data, the optical model based on Mie theory was used, assuming $n = 1.7$, $k = 0.1$ for grey clinkers, and $k = 0.001$ for white cement. The surface area was further analyzed using nitrogen sorption with Horiba SA-9600 and was analyzed using Brunauer–Emmett–Teller (BET) approach.

2.3.3 | Heat of hydration

The heat release from cement paste samples was measured at isothermal conditions using a TAM Air 8 channel calorimeter. The cement pastes are prepared by dry mixing appropriate amounts of gypsum with the clinker and then mixing with water at a w/c of 0.5. The paste was then mixed thoroughly by hand, and approximately 6–8 g of the cement paste was transferred into glass ampoules before transferring into the calorimeter. Although using a mechanical mixer is preferable for paste preparation, it was not used in this study due to the significantly larger quantity of materials it would require. The heat release was

monitored at 20°C for at least 7 days and used an ampoule with deionized water in the reference chamber.

2.3.4 | X-ray diffraction

XRD measurements were performed using a Bruker D8 Advance equipped with Cu K_{α} radiation ($\lambda = 1.54 \text{ \AA}$). It used a LYNXEYE XE-T psd detector operated at 40 kV and 40 mA. All the samples were scanned from 5° to 60° 2θ with a step size of 0.015° 2θ and a time per step of 0.3 s that took about 20 min per measurement. The measurements were carried out with a variable divergence slit (fixed sample illumination) with automatic anti-scatter screen. The anhydrous powder samples were front-press loaded before measurement. For studying hydrated pastes, cement pastes were prepared at 0.5 w/c ratio and were cured at 20°C. After 1, 2, 7, and 28 days, the hydrated pastes were cut into discs, and the surface was polished with sandpaper before measurements. Hydration stoppage or drying was not employed for any of the hydrated samples. The quantitative phase composition was determined using Rietveld analysis using Topas Academic v7. Corundum was used as the external standard, and appropriate corrections for mass absorption coefficient were taken. For the Rietveld analysis, a first-order Chebyshev polynomial along with $1/X$ term was used for refining background. The amorphous C–S–H structure was fitted using a model structure reported previously.³⁹ For crystalline phases, the unit cells, crystallite size, and the scale factor were refined. Preferred orientation corrections were applied for portlandite (0 0 2), graphite (0 0 2), and alite (6 0 –6).

2.3.5 | Electron microscopy

The microstructure and microanalysis of the clinkers were studied using electron microscopy equipped with energy dispersive spectroscopy (EDS). A Zeiss Gemini SEM was used with an acceleration voltage of 15 kV at a working distance of 8.5 mm. For EDS analysis, an Oxford UltimMax 170 EDS detector was used and was acquired and analyzed using Aztec 5.1 software. Prior to measurements, the samples were embedded in an epoxy resin under vacuum. The epoxy was uncovered using SiC paper and was polished manually using oil-based diamond sprays of 9, 3, 1, and 0.25 μm with an alcohol-based lubricating agent. Backscattered electrons (BSE) image was taken at a resolution of 2048×1536 , and EDS maps were acquired at a resolution of 256×192 with pixel dwell time of 50 μs and total acquisition time of approximately 30 min. For EDS point analysis, a process time of four was used, which in effect had a measurement of 30 s.

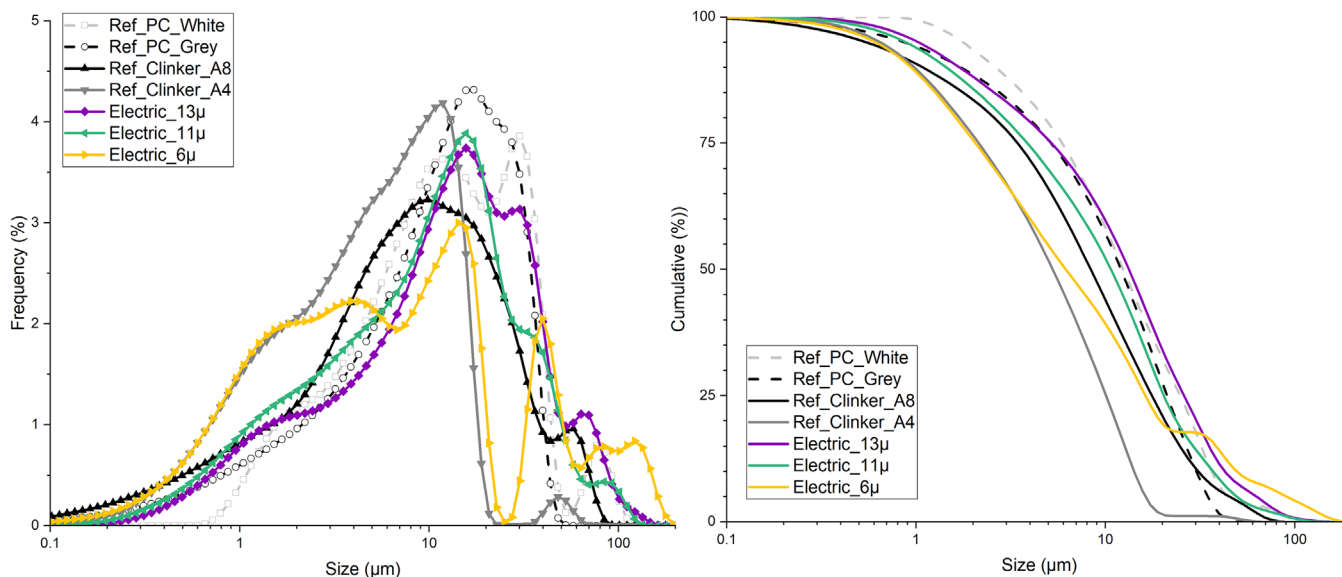


FIGURE 1 Particle size distributions measured from laser diffraction. The particle size distribution of Ref_PC_grey was adapted from.

TABLE 1 Fineness of clinkers or cement from laser diffraction and Brunauer–Emmett–Teller (BET) surface area.

	d10 (μm)	d50 (μm)	d90 (μm)	BET (m ² /g)
Ref_PC_White	2.5	12.5	36	1.8
Ref_PC_Grey	1.7	11.7	30	1.3
Ref_Clinker_A8	1.1	8.2	31	1.3
Ref_Clinker_A4	1.0	5.2	14	–
Electric_13μ	1.7	13.3	43	1.0
Electric_11μ	1.4	10.6	37	1.2
Electric_6μ	0.9	6.1	48	3.1

3 | RESULTS

This section is split into two parts as follows. The first part is a detailed physical, chemical, and mineralogical characterization of the clinkers/cements. The second part explores the reactivity of the clinker with an emphasis on the effect of gypsum content on sulfation.

3.1 | Characterization of clinker

The particle size distributions of the clinkers as well as the reference cements are shown in Figure 1 and are further tabulated in Table 1 along with the BET surface area. As the names indicate, the electric clinkers, Electric_13μ, Electric_11μ, and Electric_6μ, have d50 of 13, 11, and 6 μm, respectively. The coarser electric clinker (Electric_13μ) has similar fineness to white cement (Ref_PC_White), and the finer electric clinker (Electric_6μ) has similar fineness to

low C₃A reference clinker (Ref_Clinker_A4). The intermediate fineness electric clinker (Electric_11μ) and the higher C₃A reference clinker (Ref_Clinker_A8) had similar protocols for grinding with the same feed and thus have similar fineness, although the reference clinker appears to be marginally finer. The fineness of Ref_PC_grey, Ref_Clinker_A8, and Electric_11μ was reported in our previous work.²⁸ These measurements were repeated in the present study and found to be consistent, except for Ref_PC_grey, where the discrepancy is possibly due to agglomeration.

The mineralogical phase compositions determined from XRD/Rietveld analysis of the different clinkers and white cement are reported in Table 2. The oxide compositions measured from XRF are further reported in Table 3. Comparing the measured oxide compositions between XRF and that calculated from XRD (the method used to calculate the oxide composition from XRD is provided in Supporting Information section), some discrepancies are found for electric clinkers (Figure S1). For electric clinkers, XRD underestimated Fe₂O₃ (2.3%–4.2%) and Al₂O₃ (0.5%–0.9%) content, while overestimating SiO₂ (–1.9% to –2.7%) and CaO (–0.2% to –1.3%). The discrepancy was considerably higher for Fe₂O₃ and SiO₂ (see Supporting Information section for details). Bogue calculations are not applicable to electric clinkers produced over molten steel as iron is present in different oxidation states. XRD also confirmed the presence of oldhamite (CaS) in all the electric clinkers due to the highly reducing conditions and presence of sulfates in the feedstock. The negative LOI (Table 3), or “gain on ignition,” is explained by the presence of sulfur and iron in reduced states that would oxidize to sulfates and ferric oxides upon heating.

TABLE 2 Phase compositions from x-ray diffraction (XRD)/Rietveld analysis.

	Ref_PC_White	Ref_PC_Grey	Ref_Clinker_A8	Ref_Clinker_A4	Electric_13 μ	Electric_11 μ	Electric_6 μ
Alite M3	67.3	50.9	53.7	71.1	58.5	60.1	67.2
Belite β	15.5	19.0	23.7	6.9	23.0	19.0	13.9
Belite γ	0.4	1.4	2.0	0.4	2.6	1.5	1.5
C ₃ A cubic	2.7	8.2	7.7	4.1	8.9	8.8	9.1
Ferrite	0.2	8.4	9.6	9.9	2.4	1.5	2.7
Free lime	0.4	0.2	0.3	0.2	0.9	0.2	0.2
Periclase	0.3	0.1	0.2	0.9	0.3	0.7	0.5
Wuestite	–	–	–	–	0.1	0.2	0.2
Metallic Iron	–	–	–	–	0.7	1.0	1.1
Graphite	–	–	–	–	0.3	0.5	0.1
Oldhamite	–	–	–	–	2.0	2.3	2.5
Mayenite	0.5	0.2	0.1	1.0	0.1	0.1	0.3
Quartz ^a	0.2	0.3	0.1	0.2	0.2	2.0	0.8
CaCO ₃ ^b	6.0	5.1	–	–	–	2.2	–
Gypsum	3.5	0.7	–	–	–	–	–
Anhydrite	0.9	0.8	–	–	–	–	–
Bassanite	0.9	1.8	–	–	–	–	–
Arcanite	0.9	0.7	0.9	0.8	–	–	–
Aphthitalite	–	–	–	1.8	–	–	–
Portlandite	0.5	2.2	1.9	2.2	–	–	–

^aThe presence of quartz in electric clinkers is due to contamination during taping.

^bIn calcite form for reference, Portland cements from limestone addition; and in vaterite form in Electric_11 μ from carbonation of clinker.

TABLE 3 Oxide compositions from x-ray fluorescence (XRF) and loss on ignition.

	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	SO ₃	Na ₂ O _{eq}	LOI
Ref_PC_White	70.2	23.8	2.1	0.3	0.6	2.7	0.2	3.2
Ref_PC_Grey	66.7	20.1	5.0	3.6	1.0	2.4	0.4	3.1
Ref_Clinker_A8	66.8	21.6	5.6	3.9	0.9	0.7	0.4	0.2
Ref_Clinker_A4	66.1	20.2	4.7	3.3	2.0	1.6	0.8	1.1
Electric_13 μ	65.9	21.6	4.9	4.5	0.9	2.4	<0.1	–2.6
Electric_11 μ	64	21.7	4.7	6.5	1.3	2.4	<0.1	–2.2
Electric_6 μ	65.7	21.1	4.6	5.1	1.1	2.3	<0.1	–3.7

The electric clinkers have the C₃A content of around 9% within the typical error associated with an XRD analysis. Comparison with XRF (Figure S1) suggests C₃A might be underreported by 1%–2%. Comparing the electric clinkers to the original cement used for producing HCP, electric clinkers have a higher C₃A content and lower ferrite content, which is expected upon re-clinkering in a reducing environment.³³ For calcium silicates, the overall levels in the three electric clinkers are comparable; however, the ratio of alite to belite varies. The calcium silicate in the electric clinkers is around 3% higher than Ref_PC_grey, which could be because of the excess limestone in cement and possibly some silica dissolved in steel released to clinker.

The overall levels of calcium silicates in the three electric clinkers are comparable; however, the ratio of alite to belite varies. With increasing fineness, the alite content rises, whereas the belite content reduces. A combination of factors might be responsible for this variation, although the grinding protocol is not one of them. This is most likely due to the oxidation of the steel during the re-clinkering process. The molten steel that conducts heat for clinkering, upon contact with the ferric oxides present in HCP or air, could get oxidized. Any oxidation of steel will preferentially oxidize its dissolved silicon content, which would be picked up by the clinker, reducing the lime saturation.

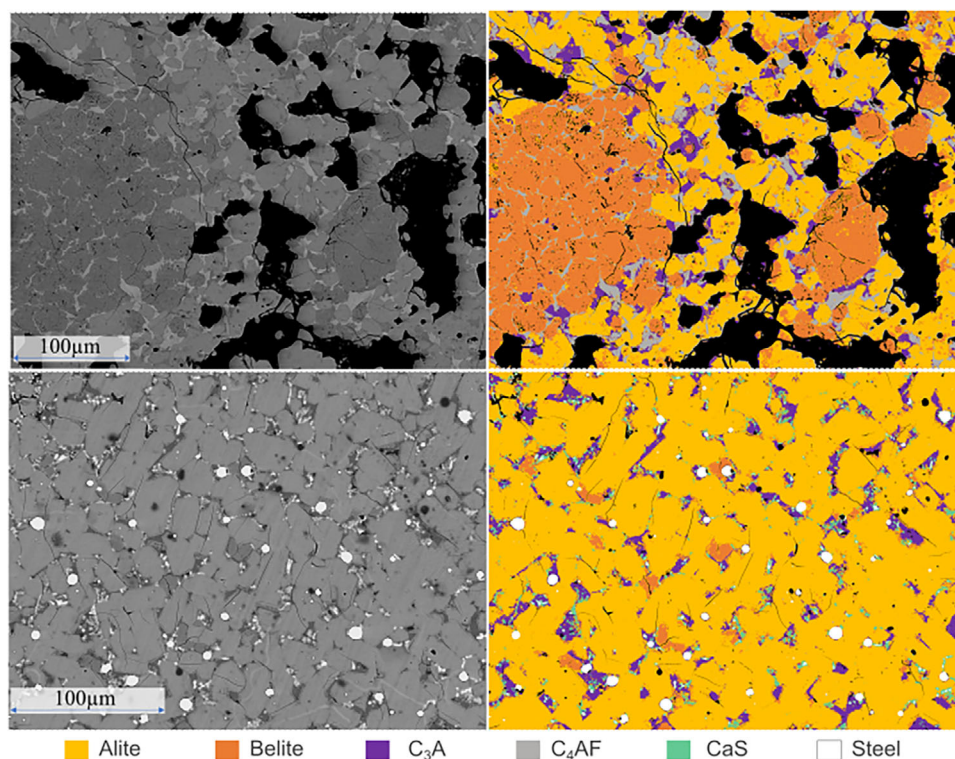


FIGURE 2 Unfiltered backscattered images (left) and processed phase segmentation aided by energy dispersive spectroscopy (EDS) mapping (right) for un-milled clinkers after impregnation in epoxy. Top: reference clinker (Ref_Clinker_A8), bottom: electric clinker (Electric_6μ).

Figures 2 and 3 show the microstructure and distribution of the different phases in the un-milled and milled clinkers, respectively. The different phases are characterized by using the grey scale levels from BSE coupled with the EDS mapping based on an approach proposed previously.^{40,41} To do this, we developed an image analysis program. The fundamental parameters that are used for phase identification are tabulated in Table S1. The grey scale values from BSE image were first used to separate different categories of phases as the brightness of different phases is dependent on their electron density. EDS elemental maps were used to differentiate among different phases. To enhance the data and reduce the noise, filters were used as summarized in Table S2. Un-milled samples were easier to polish over the milled samples, which were more challenging due to grain popouts that caused surface scratches.

Figures 2 and 3 reveal differences between the reference grey clinker and electric ones. First, alite and belite form more heterogeneously in the reference clinker compared to electric clinkers. This may be due to the feedstocks used for production as HCP would be more homogenous at microscale. Second, the interstitial of reference clinker consists of C_3A and ferrite, whereas electric clinkers do not have ferrite and have CaS instead. The C_3A also appears to be more intermixed with ferrite for the reference clinker,

which is expected as both these phases become liquid at the clinkering temperatures and are crystallized upon cooling. Third, spherical steel particles in a size range of 0.5–15 μm are observed in electric clinkers. Although magnetic separation removed some of the larger steel particles present in steel, completely removing them was difficult due to their small size and them being embedded with different phases. Finally, the reference clinker appears to have a more porous microstructure compared to electric clinker (Figure 2). This could be either attributed to the homogeneity of the feedstock or due to the higher clinkering temperature employed for electric clinkers.

The proportion of the boundary of C_3A covered by different phases was quantified using image analysis. The program uses the phase segmented images from ground clinkers, and the perimeter of composition of C_3A crystals is quantified. The pixels around the perimeter of C_3A are counted separately for each of the different phases and pores and were normalized to 100%. Figure 4 reports the results from this analysis, and the fluctuations on the stacked columns represent the deviations arising from the differences in different images.

The results reveal major differences between the reference grey clinker and the electric clinkers. The amount of alite, belite, and the pores surrounding the C_3A is notably higher for electric clinker. Furthermore, around 10% of

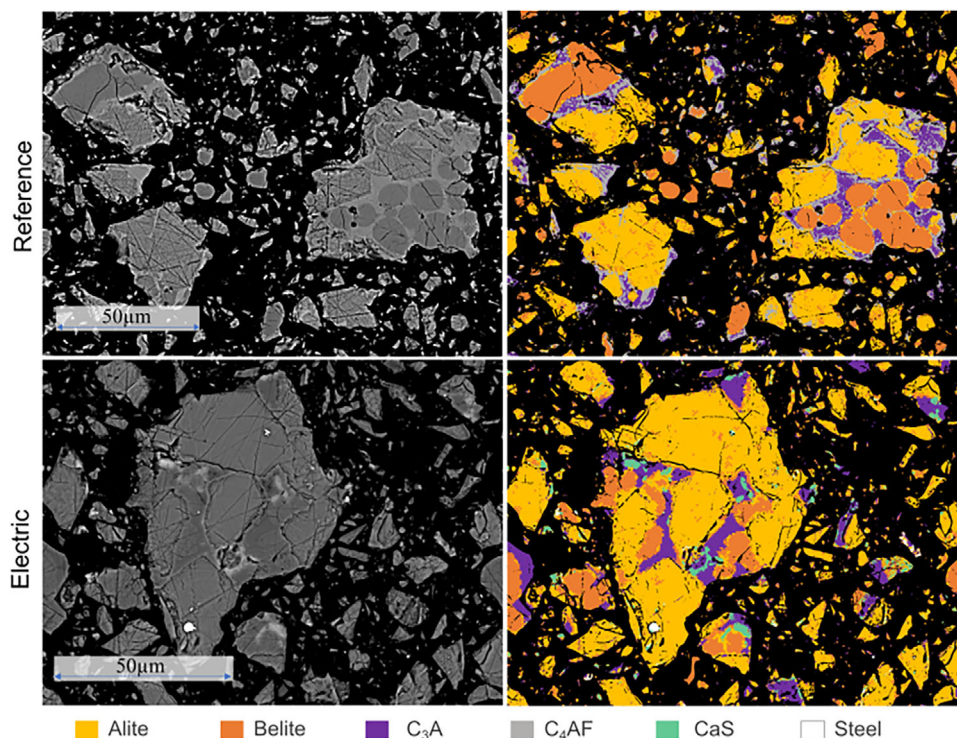


FIGURE 3 Unfiltered backscattered images (left) and processed phase segmentation aided by energy dispersive spectroscopy (EDS) mapping (right) for ground clinkers after impregnation in epoxy. Top: reference clinker (Ref_Clinker_A8), bottom: electric clinker (Electric_11μ).

the boundary of C_3A in the electric clinker was CaS . The largest difference is the presence of ferrite around the C_3A crystals in the reference clinker, which covers almost half of the C_3A surface. It should be noted that the ferrite content in the reference clinker was about only 10%. In contrast, there is no ferrite on the vicinity of C_3A for electric clinker. Previous studies have also reported C_3A being mixed with the dendritic crystals of ferrite in conventional clinkers.³¹

The composition of the major clinker phases was characterized by x-ray microanalysis. Figure 5 plots the data from EDS point analysis as ternary plots. Due to their similarity, the data points from all the three electric clinkers are plotted together.

A few distinct zones with concentrated data points are visible. In the $Ca-Si-Al$ ternary plot, the zone of high calcium concentration corresponding to white cement is due to its presence of limestone and gypsum, which does not have much silica and alumina. In the same figure, three more zones are visible, corresponding to alite, belite, and a combined zone for C_3A and ferrite. Although alite and belite have similar compositions from the various clinkers, a notable difference is visible for the C_3A -ferrite zone. The variation of the composition of C_3A -ferrite phases is better captured on the $Ca-Al-Fe$ ternary plot as it is primarily due to the variations of ferric oxides. A few points

from electric clinkers were also observed near the composition of mayenite ($C_{12}A_7$), although this may be mostly from $C_{11}A_7 \cdot CaS$, a phase reported in clinkers produced under reducing conditions.³¹ It should be noted that the figure gives no indication of the relative abundance of any phase, and traces of minor phases are expected.

The oxide composition of the major phases is plotted in Figure 6, with the average compositions along with their standard deviations summarized in Table 4. The compositions of the phases are compared against theoretical pure phase compositions and that reported by Taylor.⁴² Generally, the composition of all the phases of reference grey clinker and white cement aligns with the composition of different phases as reported by Taylor. Some discrepancies exist for white cement regarding the higher silica content in C_3A and higher alumina content in some of the belite. These differences are attributed to the large interaction volume of EDS and small C_3A crystals in white cement.

For electric clinkers, alite, belite, and C_3A had negligible dissolved alkali and iron oxide content. Further, the ferrite phase in electric clinker had considerably lower dissolved alumina. The lack of iron oxide in the calcium silicates and C_3A phases suggests that the iron is in a reduced state during clinkering reactions, and the formation of ferrite occurs during cooling, upon oxidation of Fe^{2+} or metallic iron.

TABLE 4 Molar composition of phases with standard deviations in the brackets.

	Alite	Belite	Aluminate	Ferrite
Pure phase	C ₃ S	C ₂ S	C ₃ A	C ₄ AF C ₂ F
Taylor ⁴²	C ₃ S _{0.99} A _{0.02} F _{0.01} M _{0.06}	C ₂ S _{0.93} A _{0.04} F _{0.01} M _{0.02} K _{0.02}	C ₃ A _{0.91} S _{0.18} F _{0.09} M _{0.10} N _{0.04} K _{0.02} C ₃ A _{0.96} S _{0.22} F _{0.02} M _{0.07} N _{0.02} K _{0.02} ^a	C ₄ A _{1.01} F _{0.63} S _{0.28} M _{0.35} ^b C ₄ A _{0.73} F _{0.91} S _{0.28} M _{0.34} K _{0.01} ^c
Ref_Clinker_A8	C ₃ S _{0.97} A _{0.03} F _{0.01} M _{0.04} (±C _{0.02} , S _{0.02} , A _{0.01} , F _{0.00} , M _{0.01})	C ₂ S _{0.92} A _{0.03} F _{0.01} M _{0.01} (±C _{0.03} , S _{0.03} , A _{0.01} , F _{0.01} , M _{0.01})	C ₃ A _{0.85} S _{0.20} F _{0.09} M _{0.04} N _{0.03} (±C _{0.03} , A _{0.03} , S _{0.04} , F _{0.01} , M _{0.01} , N _{0.01})	C ₄ A _{0.97} F _{0.62} S _{0.28} M _{0.27} (±C _{0.14} , A _{0.06} , F _{0.09} , S _{0.08} , M _{0.03})
Ref_PC_White	C ₃ S _{0.98} A _{0.03} M _{0.04} (±C _{0.03} , S _{0.03} , A _{0.02} , M _{0.00})	C ₂ S _{0.96} A _{0.02} M _{0.01} N _{0.01} (±C _{0.05} , S _{0.05} , A _{0.02} , M _{0.00} , N _{0.01})	C ₃ A _{0.64} S _{0.42} F _{0.02} M _{0.03} N _{0.03} (±C _{0.19} , A _{0.13} , S _{0.15} , F _{0.01} , M _{0.00} , N _{0.01})	– –
Electric	C ₃ S _{0.99} A _{0.02} M _{0.04} (±C _{0.02} , S _{0.01} , A _{0.01} , M _{0.01})	C ₂ S _{0.93} A _{0.03} M _{0.02} (±C _{0.01} , S _{0.01} , A _{0.01} , M _{0.00})	C ₃ A _{0.92} S _{0.24} M _{0.12} (±C _{0.06} , A _{0.13} , S _{0.08} , M _{0.03})	C ₄ A _{0.50} F _{1.19} S _{0.31} M _{0.18} (±C _{0.02} , A _{0.09} , F _{0.09} , S _{0.02} , M _{0.01})

^aComposition of C₃A for a white cement.^bComposition of ferrite for a normal iron cement.^cComposition of ferrite for a high iron cement.

Previous studies have also reported formation of low alumina C₂F like phases from oxidation of Fe²⁺ ions during cooling.³²

Varying ferric oxide content in C₃A was also noticeable from the Rietveld refinement of the x-ray powder diffraction data. Although all the clinkers exhibited a cubic polymorphism for C₃A, the lattice parameter varied, which changes the unit cell volume. Figure 7 shows that the lattice parameter “a” for the reference grey clinkers was approximately 15.25 Å, for white cement it was slightly lower at around 15.23 Å, and for electric clinkers, it was smallest at about 15.19 Å. The inclusion of ferric ions tends to increase the unit cell in C₃A.^{43–46} This is consistent with the iron inclusion in C₃A from Table 4. Although these differences in lattice parameters seem to be small, they are significant as XRD/Rietveld can measure the lattice parameters with high accuracy.

3.2 | Sulfation and reactivity

This section reports the results on the sulfation experiments. Figure 8 illustrates the rate of heat release from isothermal calorimetry at 20°C for the cements and clinkers. For clinkers, 4% gypsum addition was used. The early age heat release typically shows the main hydration peak of alite and peak of C₃A hydration upon exhaustion of calcium sulfates. In the reference high-C₃A cement (Ref_Clinker_A8), only a single peak was observed, without a clear distinction between alite and C₃A hydration. In contrast, the low-C₃A cement (Ref_Clinker_A4) displayed an additional shoulder peak, corresponding to the main hydration peak of C₃A. The other cements

exhibited distinct peaks attributed to either alite or C₃A hydration.

The relative timing of the occurrence of the C₃A peak with respect to the main peak of alite hydration determines the degree of sulfation. In an under-sulfated system, a narrow high intensity C₃A peak appears before the alite peak. In such systems, the alite hydration is retarded compared to a system with higher gypsum content due to the higher concentration of alumina in the pore solution^{47,48} or due to the higher uptake of alumina in C–S–H resulting in its reduction of surface area.⁴⁹ With the delay in the occurrence of the C₃A hydration peak, its intensity is known to decrease with peak broadening due to lower surface area of anhydrous C₃A particles at the time of sulfate depletion.^{50,51} In a properly sulfated system, where C₃A peak occurs immediately after the alite hydration peak, C₃A is typically observed as a shoulder peak.⁵² A temporary retardation of alite hydration following C₃A hydration has been reported, which gradually recovers, resulting in a “double-bell” peak shape for alite hydration.⁵³ In over-sulfated systems, the C₃A peak occurs significantly later, producing a broad, low-intensity peak that does not affect the shape of the alite peak. However, in this case, the overall hydration of the clinker may be reduced, potentially leading to poorer mid- to long-term performance.⁵⁴

Based on the heat release data from Figure 8, the low C₃A reference cement and the white cement appear to be properly sulfated. As a clear peak of C₃A is not visible for high C₃A cement, a more detailed investigation with different amounts of gypsum (Figure 9) confirmed proper sulfation. Further, the lack of double belled alite peaks further confirms none of the reference clinkers are

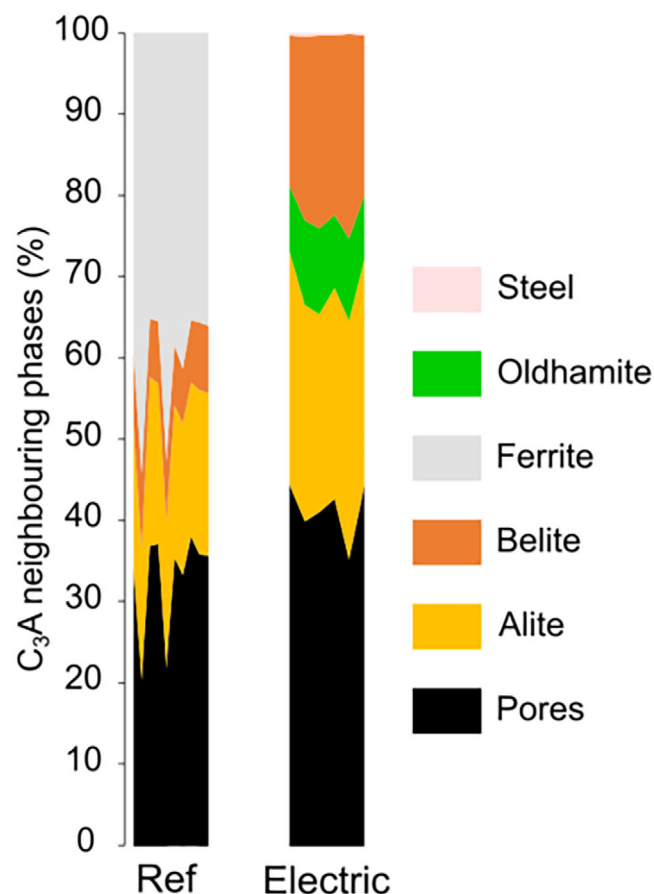


FIGURE 4 Percentage of different phases neighboring C_3A from image analysis of phase segmented images of ground clinkers. Legends: Ref. (Ref_Clinker_A8), electric (Electric_11 μ). The noise (fluctuations) within each series in the bar chart shows the results from analysis of different images. For Ref., nine images were used, and for electric, six images were used to produce the figure. This analysis only accounts for the larger crystals due to the limited resolution of EDS maps (few microns).

under-sulfated. For the electric cements, the finest and intermediate fineness ones appear to be highly under-sulfated, whereas the coarser electric cement appears to be properly sulfated. As a reference, the properly sulfated electric clinkers were also included in the figure.

Akin to Figure 9, Figure 10 shows the heat release with different amounts of gypsum for the finer electric clinker. Comparing Figures 9 and 10, some key distinct behaviors were revealed for C_3A hydration in a reference grey cement and an electric cement. The reference high C_3A grey cement is under-sulfated with 2% and 2.5% gypsum, evidenced by the earlier occurrence of C_3A peak compared to alite peak, and the peak of alite becoming broad and delayed compared to other properly sulfated systems at 4% and 5% gypsum contents. In contrast, the fine electric cement was under-sulfated even at 7.5% gypsum and appeared to be properly sulfated at 10% gypsum content.

Another major difference is the peak intensity of C_3A , which is much higher for electric cement.

Figure 10 further shows the cumulative heat release up to 39 days for the fine electric cement with 4%–12% gypsum. The under-sulfated systems have lower heat release between 8 and 24 h. However, all the systems appear to have similar heat release at later ages, consistent with previous studies.^{53,54} The lower heat release for 10% and 12% gypsum systems should be attributed to considerably lower clinker content in those mixes due to the dilution with gypsum.

To evaluate the effect of gypsum on C_3A hydration quantitatively, the C_3A hydration peak is deconvoluted from the overall hydration curve, akin to the work of Zunino and Scrivener.⁵⁵ Figure 11A shows the method of extraction of the C_3A peak using a Gaussian curve. To exclude the contribution of alite hydration, a function with two Gaussian peaks was used. The fitting of the curve was performed manually by ensuring a good visual fit, particularly around the C_3A peak. The C_3A peak height was captured from the coefficient of the Gaussian function, whereas the peak area was calculated by integrating the Gaussian curve. The peak shape was chosen for convenience, and the area calculated is expected to differ from an exact measure by 2–4 J/g. No significant error is expected for the height or location of the peak. The degree of sulfation was evaluated by comparing the position of the C_3A peak with the peak of alite on a properly sulfated system. If the C_3A peak occurs before the main alite peak of a properly sulfated system, the sulfation will be negative, and it indicates an under-sulfated system.

The results from the sulfation analysis are plotted in Figure 11B–D. Figure 11B shows the effect of gypsum content on the sulfation levels for all the clinkers and white cement as received. The hydration curves from calorimetry results are provided in the Supporting Information section. The amount of gypsum requirement for all the reference cements and clinkers appears to be around 4%–5%. For electric clinkers, the gypsum content required to achieve proper sulfation depended considerably on the fineness. The higher the fineness, the more gypsum content was required. Around 10% gypsum was required to achieve proper sulfation with the finest electric clinker. Similarly, the coarser clinker required less than 4% gypsum to achieve proper sulfation.

Figure 11C shows the peak height of C_3A plotted against sulfation. Two distinct trends are visible for either clinkers with high ferrite content (reference grey PC and clinkers) or low ferrite content (electric clinkers and reference white cement). The low ferrite clinkers had four to six times higher peak heights than the high ferrite clinkers. For all clinkers, the peak heights appear to reduce when going from a high degree of under-sulfation to proper sulfation, after which reductions are only marginal. These

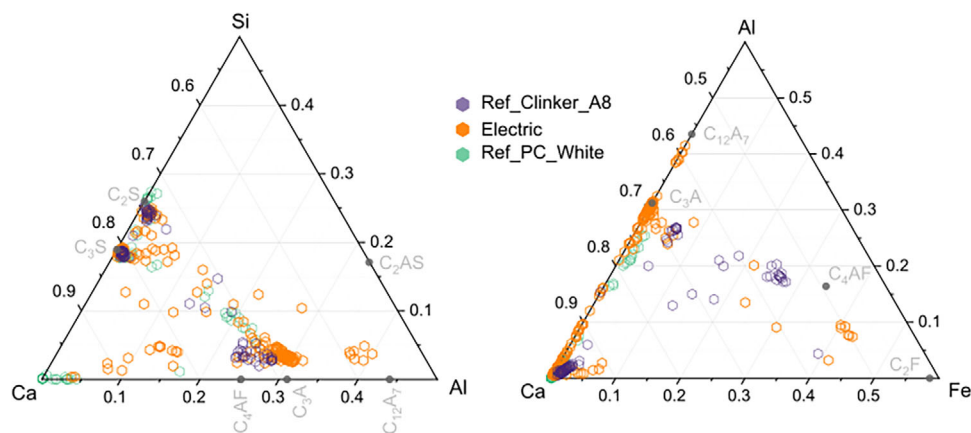


FIGURE 5 Ca-Si-Al (left) and Ca-Al-Fe (right) elemental ternary plots from EDS point analysis.

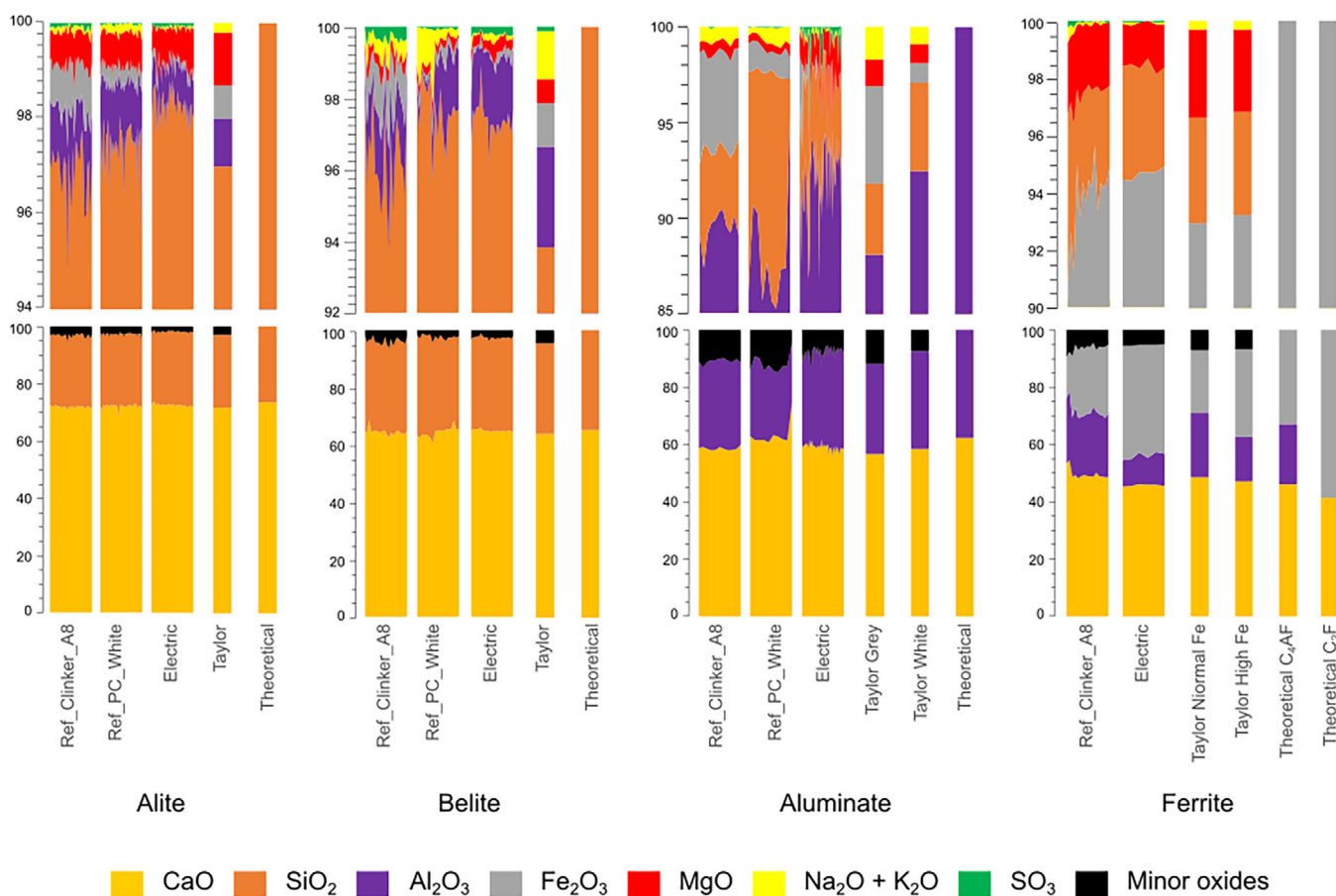


FIGURE 6 The oxide composition of the different phases from energy dispersive spectroscopy (EDS) point analysis, compared against the theoretical ideal composition and compositions reported by Taylor.⁴² The noise represents the variation among different data points.

differences were more evident for electric clinkers than reference grey clinkers.

The plot of C_3A peak area against sulfation (Figure 11D) also exhibited two separate trends depending on the amount of ferrite content. The peak area was two to four times higher for low ferrite systems. Unlike the peak height, the peak area was found to increase with increasing

sulfation for electric clinkers. For reference grey clinkers, variation was within the error for such measurement.

Quantitative measures of alite and C_3A reaction were obtained using XRD/Rietveld analysis. Figure 12 shows the evolution of degree of hydration of alite and C_3A from 1 to 28 days at a fixed gypsum content of 4% along with properly sulfated at 1 day for two highly under-sulfated

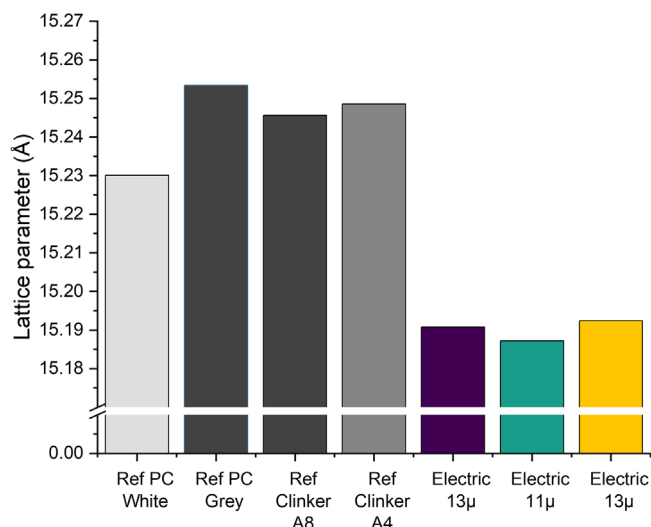


FIGURE 7 Lattice spacing of refined C_3A .

electric clinkers. Alite hydration only shows marginal deviations between the clinkers investigated. Nevertheless, the effect of fineness on the alite hydration was clearly visible for electric clinkers, particularly in the early ages. The relatively lower degree of hydration of alite for the medium-fineness electric clinker could be due to under-sulfation, as it is known to lower the degree of hydration of both alite and C_3A in the early ages.^{54,53} Although the finest electric clinker was also under-sulfated, its significantly higher fineness was sufficient to compensate for the reduced hydration.

On C_3A hydration, clinkers with high ferrite content appear to have considerably lower degrees of reaction in the early ages. Even after 7 days of hydration, the reference grey clinkers have a degree of hydration lower than 80%, whereas others are almost fully reacted. The effect of under-sulfation on C_3A hydration appeared to be mirroring that of alite. The under-sulfated intermediate fineness electric clinker had the lowest degree of hydration among the low ferrite clinker, whereas the fine electric clinker had similar degree of hydration to that of coarse electric clinker. Nevertheless, the degree of hydration was found to be correlating well with the fineness, once they are properly sulfated. White cement had the highest degree of C_3A hydration at the early ages. Complete hydration of C_3A in white cement within the first 2 days is often reported in literature.^{56,57}

4 | DISCUSSION

The C_3A -gypsum hydration may be divided into two periods: In the initial period, C_3A reacts slowly due to the blocking of its reactive surface by the adsorbed calcium

and sulfate ions.^{58–61} Subsequently, with the exhaustion of gypsum, adsorbed ions are consumed, and the dissolution is further enhanced, resulting in a hydration peak.^{51,60} Appropriate amounts of calcium sulfate sources are added to control this hydration peak of C_3A . If the C_3A peak occurs before the peak of alite hydration, the early age performance is affected, whereas with the addition of too much calcium sulfate, the later age performance is known to be affected. To be properly sulfated, the C_3A peak should not occur before the peak of alite hydration. If it occurs earlier, alite hydration retards leading to lower degree of hydration in the early hours or days.

The reference grey clinkers, including the grey PC, were properly sulfated at 4%–5% gypsum content. This is consistent with what is practiced in the industry, where the calcium sulfate addition is typically 3%–5% and commercial cements are always well sulfated. Interestingly, the gypsum requirement for proper sulfation varies considerably for electric clinkers depending on fineness. The gypsum requirement was less than 4% for coarser electric clinker, whereas a staggering 10% was required for the finer clinker. Such variations of gypsum requirement upon just variation in fineness are uncommon.

A common notion is that sulfation is dependent on the C_3A content in clinker and is further dependent on the clinker fineness.⁵⁴ In the present study, electric clinkers have C_3A content of around 9%, whereas the grey PC and one of the grey clinkers have around 8% C_3A content, a small difference. Recently, Enders et al.³⁴ reported a study that investigated clinkers with different C_3A contents (3.7%–10.7%) at varying fineness. Based on isothermal calorimetry results, all of the clinkers appear to be properly sulfated with an addition of 4% gypsum. This suggests electric clinkers that behave differently on C_3A reactivity compared to commercial Portland clinkers. It should be noted that increase in gypsum demand for proper sulfation does not always indicate higher C_3A reactivity, as this may result from various factors. For, for example, C–S–H is known to adsorb sulfate, and intergrinding of gypsum with clinker reduces gypsum demand.

The increase in C_3A reactivity was confirmed by the increased peak height and area of C_3A hydration (Figure 11C,D). In commercial grey Portland cements (with various compositions and fineness), the C_3A peak typically occurs as a short shoulder peak immediately after alite hydration and sharp C_3A peaks are hardly seen. However, white cements typically exhibit much stronger hydration peak of C_3A despite having low amounts of the phase.^{62,63} Strong C_3A hydration peaks are also commonly seen with synthetic model clinkers consisting of only alite and C_3A as well.^{47,53,54}

Indeed, the degree of hydration of C_3A , quantified from XRD directly shows higher reactivity in electric clinkers

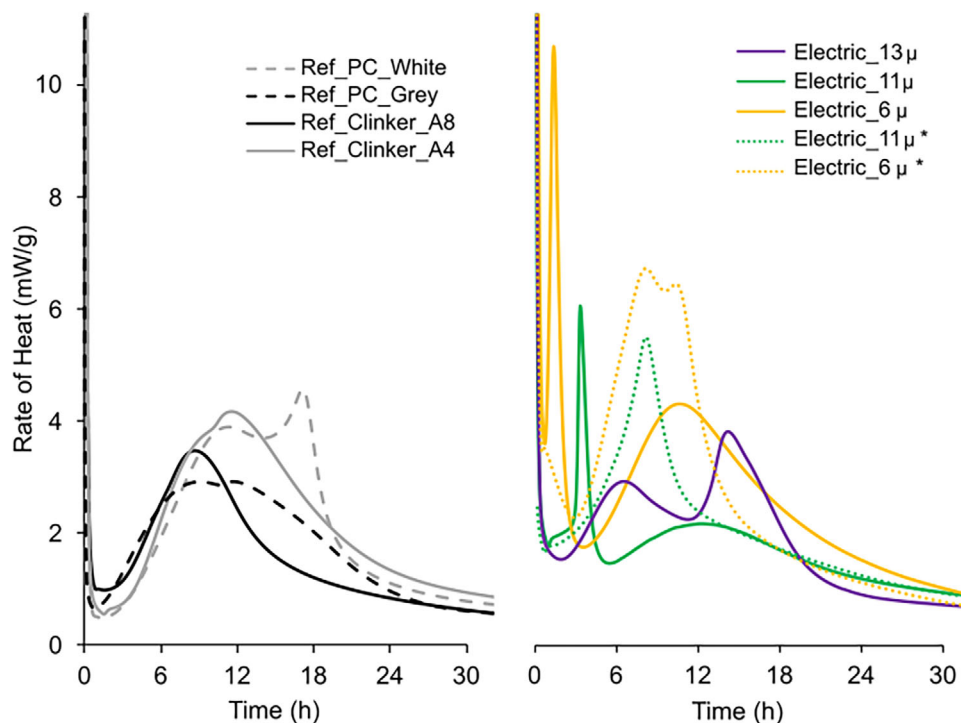


FIGURE 8 Rate of heat release for white cement and other clinkers mixed with identical 4% gypsum additions at 0.5 w/c ratio and hydrated at 20°C. *Additional properly sulfated calorimetry results for Electric_11μ and Electric_6μ with gypsum additions of 6% and 10%, respectively.

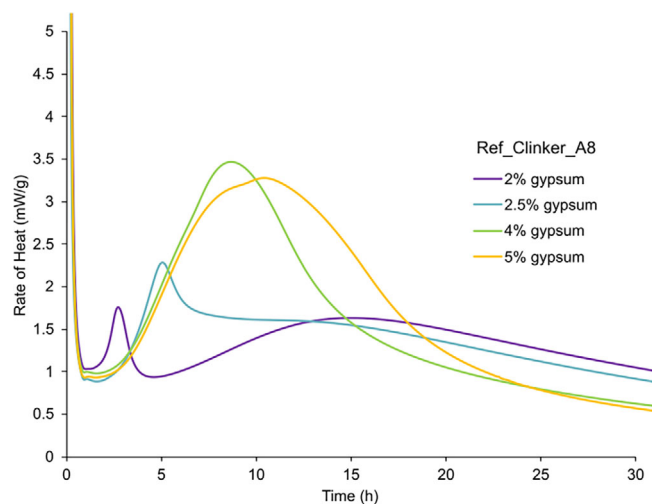


FIGURE 9 Rate of heat release for reference clinker with 8% C_3A content at different gypsum contents.

compared to reference grey clinkers (Figure 12b). This is particularly evident in the early ages, after 1 and 2 days of hydration. The differences in the degree of hydration of alite and C_3A show that this is not just an effect of fineness.

Overall, this indicates that the clinkering process can cause C_3A to be more reactive in certain circumstances. As the C_3A in electric clinkers and white cement is more reactive than the reference grey clinkers, two major questions

arise as follows: First, why is it more reactive, and second, what are the implications for practical applications? These questions are addressed separately in the following discussion.

4.1 | Why is C_3A more reactive in certain clinkers?

Table 5 summarizes some key findings from the current study. Comparing the cement characteristics and reactivity, a key aspect that is obvious is the effect of iron oxide in the interstitial on the reactivity of C_3A . Both white cement and electric clinkers with low ferric oxide contents have considerably higher C_3A reactivity. Previous studies on model cements with polyphase C_3S - C_3A clinkers, which lack ferric oxides, also demonstrated sharp hydration peaks for C_3A based on isothermal calorimetry results.^{47,54} They further reported high degrees of hydration of C_3A (>65%) after 1 day of hydration.

Although ferrite has low reactivity, during Portland cement production, it increases the melt content that accelerates alite formation and makes cement production cheaper. White cements have negligible ferrite content as the low iron content ensures whiteness of the clinker. The low melt content in such clinkers requires higher temperature production and expensive mineralizers (such as

TABLE 5 Key findings from the study.

		Ref_PC_White	Ref_PC_Grey	Ref_Clinker_A8	Ref_Clinker_A4	Electric_13 μ	Electric_11 μ	Electric_6 μ
Characterization	Fineness— d_{50} (μm)	12.4	2.9	8.4	5.3	13.3	10.7	6.2
	C ₃ A content (%)	2.7	8.2	7.7	4.1	8.9	8.8	9.1
	C ₃ A polymorph	Cubic	Cubic	Cubic	Cubic	Cubic	Cubic	Cubic
	C ₃ A mixed with ferrite	No	Yes	Yes	Yes	No	No	No
	C ₃ A crystal size ($\text{\AA}$)	15.23	15.25	15.25	15.25	15.19	15.19	15.19
	Fe ³⁺ in C ₃ A	1.2	5.2 ^a	5.2	5.1 ^b	0.5	0.5	0.5
Performance	Gypsum for PS ^c (%)	5	4	4	4	4	6	10
	C ₃ A peak height (mW)	2	0.5	0.5	0.5	4.3	2.1	1.9
	C ₃ A peak area (J)	16.6	7	6.4	5.7	20.6	13.4	12.6
	C ₃ A DoH 1d (%)	83	30	27	42	65	70	72

^aAssumed to be same as Ref_Clinker_A8 as they are from the same cement plant.

^bBased on Taylor.⁴²

^cProper sulfation

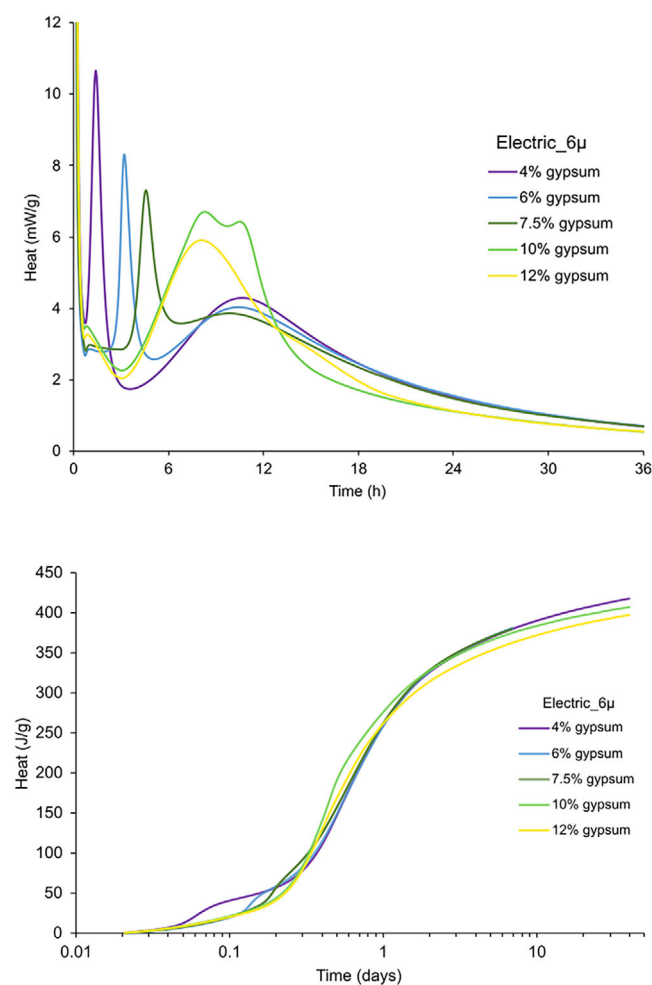


FIGURE 10 Rate (top) and cumulative (bottom) heat release for the fine electric clinker (Electric_Fine) at different levels of gypsum contents.

fluorspar), leading to lower kiln output and thus higher cost and fuel requirements. Although higher melt content could also be achieved by increasing the alumina content, this could reduce durability, increasing the susceptibility to sulfate attack. Standards around the world commonly limit the maximum C₃A content. As the interstitial phases are formed upon cooling the melt content, C₃A and ferrite, which is liquid at clinkering temperatures, become considerably intermixed. Indeed, the microstructural characterization showed that in the reference grey clinkers, C₃A was mostly covered by ferrite (Figures 2–4) as observed in earlier studies.⁶⁴ Ferrite phases with low reactivity could block the progression of the dissolution of C₃A or delay new dissolution fronts. In contrast, as can be seen from Figures 2 and 3, the C₃A in electric clinkers are without intermixing with ferrite.

As C₃A is inherently more reactive than other phases in Portland cement, other phases, such as alite and belite, will also block the C₃A dissolution front and limit the C₃A degree of hydration in the early ages. Quennoz and Scrivener⁴⁷ have reported the difference in reactivity of C₃A in a monophase system versus polyphase system. In a monophase system, the alite and C₃A individual grains are mixed, whereas in a polyphase system, both these phases are present in the same grain as in clinker. It was shown that a polyphase system with similar fineness to a monophase system had considerably less intense C₃A hydration peak, as evidenced by the C₃A hydration peaks of their individual systems at the same gypsum content. This shows that even a highly reactive phase such as alite can hinder the reactivity of C₃A by acting as a physical barrier. This also explains the considerable difference in the C₃A reactivity for electric clinkers at different fineness. With increasing fineness, more C₃A

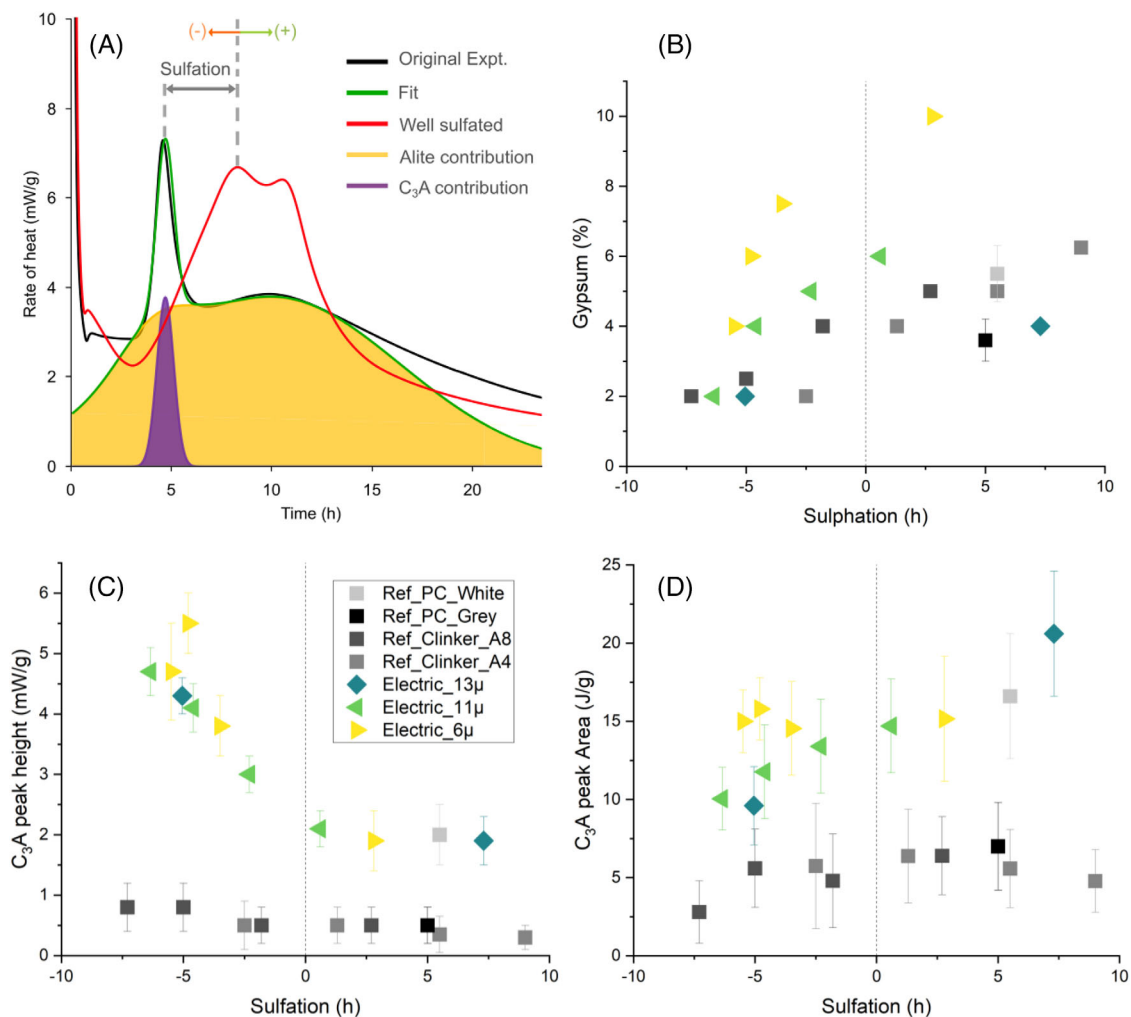


FIGURE 11 Heat released by the aluminate reaction measured by peak deconvolution and numerical integration. (A) The C₃A peak was identified by the deconvolution of the hydration peaks as measured by isothermal calorimetry. The heat released is assumed to come from the dissolution of C₃A and C₃S. The sulfation is measured as the difference between the occurrence of the main peak of C₃A and a well-sulfated peak of alite; (B) effect of gypsum content on sulfation; (C) C₃A peak heights plotted against sulfation; (D) C₃A peak area plotted against sulfation.

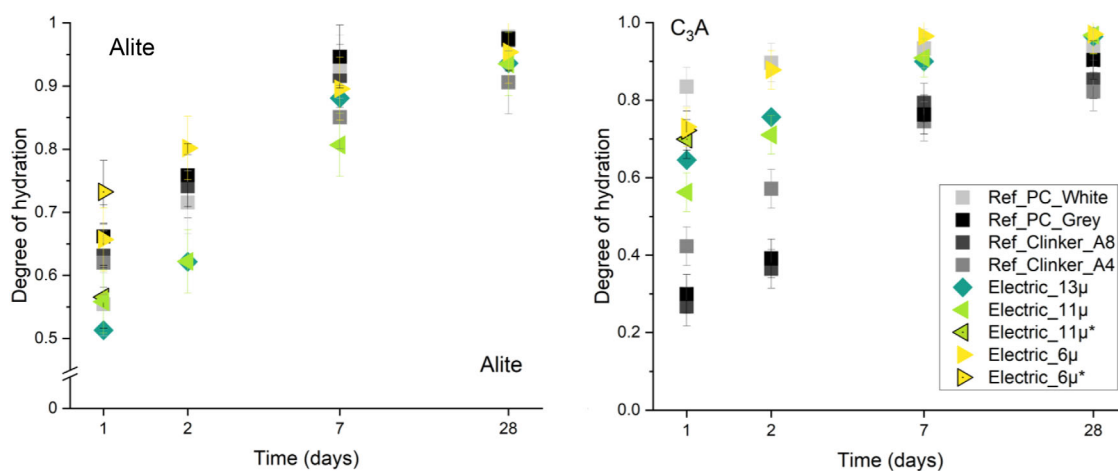


FIGURE 12 Degree of alite (left) and C₃A (right) hydration as measured by x-ray diffraction (XRD) for reference white cement and with 4% gypsum content for clinkers. *Additional properly sulfated 1 day XRD results for Electric_11μ and Electric_6μ with gypsum additions of 6% and 10%, respectively.

particles will be available for reaction, and they will be less blocked by alite and belite phases. In a grey Portland clinker, this effect is limited as C_3A is mostly covered by ferrite by intermixing at sub-micron scale. Although not as remarkable as in electric clinkers, some effects of C_3A hydration with increasing fineness have also been reported for conventional Portland cements.^{34,65}

A second factor for the enhanced reactivity of C_3A could be its inherent higher reactivity for clinkers with low Fe_2O_3 content. Stephan and Wistuba⁴⁵ studied the effect of doping of different oxides on the crystal structure and its reactivity. Of the different oxides they investigated, the influence of Fe_2O_3 was found to be the highest. With increasing Fe_2O_3 content in C_3A , a systematic decrease in the reactivity was clearly visible. This also altered the crystal structure of C_3A as evidenced by the changes in lattice parameters as measured by XRD. As the electric clinkers and white cement had low Fe_2O_3 content in C_3A , they would thus have higher intrinsic reactivity compared to the C_3A in reference grey clinkers. In reality, it would not be one factor or another, but a combined effect of both ferrite blocking the reactive C_3A surface and lower intrinsic reactivity of C_3A due to the crystal structure modification with ferric ion incorporation.

4.2 | Practical implications due to higher C_3A reactivity

The major concern with increasing C_3A reactivity is the requirement for additional gypsum to ensure proper sulfation. High degrees of under-sulfation could induce fast setting that would reduce the available time for concrete made from such cements to be transported and placed for in situ applications. Further, as under-sulfation is known to retard alite hydration, this could also lead to lower performance, particularly at early age.

Although gypsum has only marginal emissions, and increasing the gypsum content reduces the overall emissions associated with cement, there are limitations imposed by standards on the maximum sulfate content. The European standard, EN 197-1, limits the maximum sulfate content to be 3.5% for 32.5 N and R, 42.5 N; 4% for 42.5 R, 52.5 N and R. This is further reduced by 0.5% for sulfate resistant cement. The American standard, ASTM C150, imposes 3%–3.5% sulfate limit based on the C_3A content in cement, and restricts to maximum 2.3% for sulfate resistant cement. The Indian standard IS 269-2015 limits the sulfate content to 3.5%.

Therefore, the best approach would be to blend the cement with supplementary cementitious materials (SCM). In our previous paper,²⁸ we demonstrated it is possible to blend the cement to produce a limestone calcined

clay cement (LC^3) with a clinker content of only 50%. In those systems with blended electric clinkers, the strength was significantly higher than for neat cements, motivating further exploration of blending with other SCMs. Upon blending, the overall sulfate content reduces, as both the sulfides present in the clinker and the gypsum required for sulfation reduce due to dilution of clinker. For example, the Electric_11 μ clinker becomes properly sulfated in a LC^3 composition of 50% clinker, 30% metakaolin, 15% limestone, and 5% gypsum (Figure S2). The overall SO_3 content in this cement was 3.5%, including the sulfides present in cement. In contrast, a properly sulfated cement with Electric_11 μ clinker requires 6% gypsum content for proper sulfation, which would make the total SO_3 content 5.2%.

At present, the most used SCMs are limestone, ground granulated blast furnace slag (GGBFS), fly ash, and calcined clays. Among them, GGBFS is known to have around 2%–3% equivalent sulfate content in the form of sulfides, and class F fly ash typically has less than 2% sulfates⁶⁶ and may be lower than 0.2% depending on the source.⁶⁷ Limestone and calcined clays typically have less than 0.1% sulfate content.⁶⁸ Although calcined clays are known to increase the sulfate demand when blending with Portland cement,⁶⁹ this will still keep the overall sulfate content in the blended cement within the requirements of the norm due to the dilution effect. Due to the filler effect,^{70,71} SCMs accelerate the hydration of alite preferentially compared to C_3A , which further helps with sulfation, although additional C–S–H precipitation could adsorb more sulfates.⁴⁷

5 | CONCLUSION

Electric cements produced in reducing conditions are found to have increased reactivity of C_3A . This is evidenced by the strong peak of C_3A from isothermal calorimetry and significant increase in degree of hydration measured from XRD. The gypsum requirements for making these clinkers properly sulfated are found to be high, particularly when the clinker is ground fine. Although there are different ways to properly sulfate the clinker, staying within the limits proposed by the norms, the most efficient strategies would be by either adjusting the fineness or by blending the clinker with SCMs.

In this work, we showed that two factors are critical for the kinetics of reaction of C_3A , both of which are linked to the ferric oxide content in the clinker. The first factor is the physical location of C_3A within the clinker. Mostly ferrite, but to some extent also belite and alite, form a physical barrier preventing the dissolution and reaction of C_3A as they are orders of magnitude less reactive than C_3A . Ferrite in

particular can form a solid solution with C_3A at clinkering temperatures and thus is more intermixed. The second factor is the integration of Fe^{3+} ions in the crystal structure of C_3A , affecting its intrinsic reactivity.

Although some ferrite phases were found in electric clinkers, they were not intermixed with C_3A , so they do not act as a barrier for C_3A dissolution, and Fe^{3+} ions were not incorporated in C_3A .

Together, these results indicate that iron oxides play an important role in the kinetics of reaction of Portland cement, despite not being themselves reactive. This could also explain why model systems exhibit significant deviation from the behavior of Portland cements of nominally the same compositions.

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CONFLICT OF INTEREST STATEMENT

Shiju Joseph, Rohit Prajapati, and Cyrille Dunant report a relationship with Cambridge Electric Cement Limited, including consulting, employment, and equity or stocks. Julian M. Allwood reports a relationship with Cambridge Electric Cement Limited: equity and stocks. Cyrille Dunant and Julian M. Allwood have patent #US20240318271A1 pending to Cambridge Enterprise Ltd.

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SUPPORTING INFORMATION

Additional supporting information can be found online in the Supporting Information section at the end of this article.

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