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# Effect of Lanthanides on the Mineralogical Composition of Portland Clinker Accessed by Thermodynamic Modelling

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***Abstract*** - The development of sustainable production has motivated using alternative raw materials in Portland cement manufacture. Co-processing industrial by-products containing impurities can change the stability of the clinker phases. Several studies have explored the effect of minor elements in the clinkering process. However, the effect of lanthanides remains unclear. This class of elements has been scarcely investigated due to its limited content in conventional alternative materials. Nevertheless, the increasing co-processing of by-products from the oil industry containing lanthanides demands further investigations on the effects of these elements. Furthermore, using alternative raw materials demands extensive experimental programs and investing time and financial resources. In this context, this study uses thermodynamic modelling to evaluate the effect of lanthanides on Portland clinker production. Systems containing La, Ce, Eu, Gd, Pr, and Nd as oxides in up to 10 wt.% of clinker raw meal processed at 1200 and 1400 °C were simulated. Thermodynamic calculations were based on the Gibbs energy minimisation method and performed in the FactSage software. La, Pr, Eu, Nd, and Gd improved the clinker $C_3S$ content. This effect was more significant for up to 3 wt.% of added dopant. These elements stabilised $C_2(A,F)$ rather than $C_3(A,F)$, suggesting a possible application in manufacturing high-ferrite and sulphate-resistant cements. $Ce_2O_3$ promoted notably different behaviour on phase assemblage, decreased the $C_3S$ development, and depleted $C_2(A,F)$. The cubic perovskite was the main solid phase incorporating the lanthanides, forming $LaAlO_3$, $NdAlO_3$, $PrAlO_3$, $EuAlO_3$, or $GdAlO_3$. According to thermodynamic modelling, the co-processing of raw materials containing lanthanides can be environmentally safe since the emission of polluting gases containing impurities was negligible even when co-processing 10 wt.% of lanthanide oxide in the clinker raw meal.

***Keywords:*** Clinker, Cement, Thermodynamic modelling, Dopants, Lanthanides.

## 1. Introduction

The cement industry is responsible for high environmental impacts. The exploitation of natural raw materials can lead to resource depletion, deforestation, soil destabilisation, and other harmful effects [1]. In this scenario, the co-processing of industrial by-products in cement manufacture reduces the extraction of natural sources, promotes proper waste disposal, and often improves sustainability in production [2]. However, it is noteworthy that these by-products contain elements besides those essential for the Portland cement composition (Ca, Si, Fe, Al, O), which can alter the phase development during production.

Several studies have explored the co-processing of alternative raw materials in Portland clinker production [3]–[6]. This approach can improve manufacturing sustainability and product properties by optimising clinker composition and burnability [7]. On the other hand, the presence of potentially contaminating elements can promote limitations in the production process on an industrial scale, change the stability of clinker phases, emission of polluting gases during clinkering, and contaminate the environment by the leaching of hazardous compounds [3], [8]. In this sense, the co-processing of alternative raw materials should always be associated with studying the effects of impurities in the clinker phase assemblage and the environmental risk assessment.

The solidification of metals in clinker was reported as altered by the added content, industrial technology, processing time, and other impurities [9], [10]. The presence of non-metals can reduce the stabilisation temperature of $Ca_2SiO_4$ polymorphs, altering the hydraulicity of the cement and the mechanical properties of the pastes [11]. Several studies have investigated the effect of alkaline and transition metals on the stability of aluminates and their polymorphs [12], [13]. Although extensive research has been carried out on the effect of metals and non-metals on clinker, the presence of lanthanides needs further investigation.

The limited number of research on the influence of lanthanides in clinker production was justified by the restricted contents of these elements in ordinary alternative materials (< 0.1 wt.%) [14]. However, the increasing volume of waste from the oil industry being co-processed in cement kilns in recent years demands new investigations addressing the effect of these impurities on clinkering and gas emissions. As an example, lanthanum and cerium oxides comprised up to 5.1 and 1.6 wt.% of the spent fluid catalytic cracking catalyst (SFCC), respectively [15], [16]. SFCC was co-processed in previous investigations to replace bauxite in clinker production [4]–[6]. Nevertheless, the findings examine neither the effects of lanthanides on the clinker mineralogical composition nor their emission potential during clinkering.

Understanding the action mechanisms of lanthanides can be technologically challenging. It demands the execution of an extensive and complex experimental program, consuming financial resources, and time. In this sense, thermodynamic modelling is a useful solution. It applies the Gibbs energy minimisation principle to estimate the clinker composition throughout manufacturing. Previous investigations have established it as an accurate tool for phase determination [17], [18]. Modelling allows for optimising experimental approaches by analysing the effect of dopants on the composition of solid, liquid, and gaseous phases along clinkering [19]–[21]. It was applied to evaluate the effect of FeO, $K_2O$, MgO, $Na_2O$, $SiO_2$, $SO_3$, and $TiO_2$ [22]–[24]. However, further investigations could broaden the understanding of the effect of lanthanides incorporated in clinker raw meals due to the co-processing of alternative raw materials.

In this sense, this study applies thermodynamic modelling to investigate the influence of lanthanides on Portland clinker production. The effects of impurities on the stability of silicates and aluminates were investigated, in addition to the formation of new compounds and the polluting gases emission.

## 2. Methodology

### 2.1. Thermodynamic modelling

Thermodynamic modelling was adopted to estimate the mineral composition of the clinkers produced in the theorical study. The software FactSage version 8.2 were applied to simulations. It contains optimised model parameters for the Gibbs free energy minimisation of solution phases to clinker equilibrium calculations [19]. Thermodynamic databases for gaseous components (FactPS) and oxides in solid, liquid, and solution phases (FToxid) were used for calculating the phase assemblage during production [19], [20]. The system pressure was fixed at 1 atm and the firing temperature was 1400 °C. As input data, the composition of clinker raw meal for an ordinary Portland cement (OPC) (69.5% CaO, 22.0% $SiO_2$, 5.0% $Al_2O_3$, and 3.5% $Fe_2O_3$) was used. The lanthanides were added individually as oxides ($La_2O_3$, $Ce_2O_3$, $Eu_2O_3$, $Gd_2O_3$, $Pr_2O_3$, and $Nd_2O_3$) in up to 10 wt.% of the raw meal in 0.5 wt.% increments. The influence of dopants on the phase assemblage was evaluated at 1200, 1300, and 1400 °C during clinkering. The processing was applied using the software Equilibrium module and adopting the entire set of products available in the system. Calcium silicates are quantified as $Ca_3SiO_5$ ($C_3S$) and $Ca_2SiO_4$ ($C_2S$). Thermodynamic modelling using FactSage considers solid solutions of calcium aluminium ferrites, such as $Ca_2(Al,Fe)_2O_5$ ($C_2(A,F)$, and $Ca_3(Al,Fe)_2O_6$ ($C_3(A,F)$) [17], [19], [20]. Where (Al,Fe) means Al and Fe are variable in the structure. The modelled solid solution $C_2(A,F)$ is mainly associated with the OPC ferrite content, $Ca_2(Al_xFe_{1-x})_2O_5$, often named as $C_4AF$ [25]. The tricalcium aluminate or $C_3A$ ($Ca_3Al_2O_6$) content is included in the $C_3(A,F)$ solid solution, and the complementary content corresponds to intermediate phases in the development of $C_4AF$ [20]. Thermodynamic modelling allowed quantifying other solids, including free calcium oxide (CaO) and new compounds formed from the chemical combination of lanthanides ($LaAlO_3$, $NdAlO_3$, $PrAlO_3$, $EuAlO_3$, $GdAlO_3$, $Gd_4Al_2O_9$, $CeO_2$, $Ce_6O_{11}$, and $Ce_{18}O_{31}$) [19]. The calculated liquid phase corresponded to the melt phase content formed during clinkering. The melt fraction is mainly developed through the melting of aluminates ($Ca(Al,Fe)_2O_4$, $Ca_2(Al,Fe)_2O_5$ and $Ca_3(Al,Fe)_2O_6$) from 1250 °C, reaching their maximum at the final clinkering temperature and then resolidifying during clinker cooling [14], [25]. This study focused on analysing the effect of lanthanides during heating on clinker production (1200, 1300, and 1400 °C). The emission of compounds containing lanthanides was identified by quantifying gaseous phases during clinkering at 1400 °C through thermodynamic calculations on FactSage.

## 3. Results and discussions

### 3.1. Composition of an Ordinary Portland Clinker (OPC) during heating

Table 1 presents the composition of an OPC at different temperatures to illustrate the phase evolution in an undoped system. Tricalcium silicate ($C_3S$) is the main phase of OPC, responsible for the early-age compressive strength of hydrated cement [2]. It is formed during clinkering after 1250 °C and obtained through the reaction between dicalcium silicate ($C_2S$) and calcium oxide (CaO) [14]. $C_2S$ is generally the first silicate formed in clinkering. This compound increases the later-age compressive strength of cementitious materials [2]. Modelling using FactSage identifies its gamma ($T < 735$ °C), alpha prime (735~1435 °C), and alpha ($T > 1435$ °C) polymorphs [25]. If the system has free CaO, it combines with $C_2S$ at about 1280 °C to form $C_3S$ [14]. This reaction is verified in Table 1, where CaO is depleted at 1300 and 1400 °C as $C_3S$ increases.

Table 1. Predicted ordinary Portland clinker composition during clinkering at 1200, 1300 and 1400 °C.

| Composition (wt.%) | Phase | 1200 °C | 1300 °C | 1400 °C |
|---|---|---|---|---|
| $Ca_3SiO_5$ | $C_3S$ | 0.00 | 68.64 | 76.26 |
| $Ca_2SiO_4$ α’ | $C_2S$ α’ | 63.07 | 11.29 | 3.39 |
| $Ca_2(Al,Fe)_2O_5$ | $C_2(A,F)$ | 2.36 | 1.59 | 0.00 |
| $Ca_3(Al,Fe)_2O_6$ | $C_3(A,F)$ | 17.54 | 18.48 | 0.00 |
| CaO | CaO | 17.03 | 0.00 | 0.00 |
| Melt | Melt | 0.00 | 0.00 | 20.35 |

During heating, the proportion of $C_3(A,F)$ tends to be higher than $C_2(A,F)$. However, previous investigations have shown that this ratio tends to reverse during cooling [17]. The reason is the combination of CaO dissolved in the melt phase with $C_2S$ forming additional $C_3S$ [14]. Thereby, Ca availability is reduced for aluminates, promoting the formation of $C_2(A,F)$ instead of $C_3(A,F)$. In this sense, although the modelled OPC has a high content of $C_3(A,F)$ during heating at 1200 and 1400 °C, the system tends predominantly to form $C_2(A,F)$ during cooling [17]. At 1400 °C, $C_2(A,F)$ and $C_3(A,F)$ reached the melting point and then were converted to the melt phase.

### 3.2. Composition of lanthanide-doped clinkers at 1200 °C

Previous investigations established that the lanthanides would act similarly on the stability of the clinker phases due to their comparable atomic characteristics [14]. However, thermodynamic modelling indicated that Ce promotes notably different behaviours on the phase evolution during clinkering. On the other hand, La, Pr, Eu, Gd and Nd indeed have similar trends. Fig. 1 shows the effect of lanthanide type and content on the phase assemblage during clinkering at 1200 °C. Fig. 1a presents the data for La e as a representation of Pr, Eu, Gd, and Nd for simplification purposes, as the effect of these other lanthanides was similar.

La, Pr, Eu, Gd, and Nd stabilised $C_2(A,F)$ rather than $C_3(A,F)$. Clinkers start from 2.4 wt.% $C_2(AF)$ and reach up to 8.2 wt.% when the dopant content is maximised (Fig. 2a). For $C_3(AF)$, the content varies from 17.5 wt.% to values below 1.1 wt.%. This behaviour indicates that the presence of lanthanides promotes the formation of clinkers rich in $C_4AF$. This characteristic is particularly promising for producing high ferrite clinker, in which the $C_3A$ content is limited, to guarantee the requirements of resistance to abrasion and attack by sulphates [26]. The evolution of calcium aluminium-ferrite according to the $Ce_2O_3$ content stands out among the analysed lanthanides (Fig. 2b). Ce destabilised $C_2(A,F)$ by depleting it when 1.8 wt.% $Ce_2O_3$ was added. $C_3(A,F)$ is partially reduced as the dopant increases. Ce acted as a flux, lowering the melting point, and gradually increasing the melt phase content up to 6.1% $Ce_2O_3$.

Co-processing impurities in cement kilns promote the formation of compounds beyond those commonly found in OPC. Fig. 1 presents the new solid phases of the modelled systems with up to 10 wt.% of dopants. La, Pr, Eu, Gd, and Nd were incorporated as cubic perovskite containing Al and O. The doped systems indicated the formation of $LaAlO_3$, $PrAlO_3$, $EuAlO_3$, $GdAlO_3$, and $NdAlO_3$ with increasing values as the dopant content is increased. Previous investigations reported the formation of cubic lanthanum aluminate at temperatures above 540 °C [27], which can be pseudo-cubic or rhombohedral under industrial conditions [28]. Although the modelled structure of $PrAlO_3$ was cubic, this compound has the highest number of crystalline structure transitions among rare earth perovskites [29]. $NdAlO_3$ and $GdAlO_3$ were classified as materials with high optical conductivity, applicable in producing optical amplifiers and solar panels [30], [31]. For Gd, doping above 8 wt.% resulted in the destabilisation of $GdAlO_3$ and the formation of $Gd_4Al_2O_9$. This phase was synthesised in previous research by processing $Gd_2O_3$ and $Al_2O_3$ at temperatures ranging between 1400 and 1700 °C [32]. $Gd_4Al_2O_9$ is classified as an enhancer of the mechanical properties of ceramic materials, including the toughness and fracture strength of brittle ceramics [33].

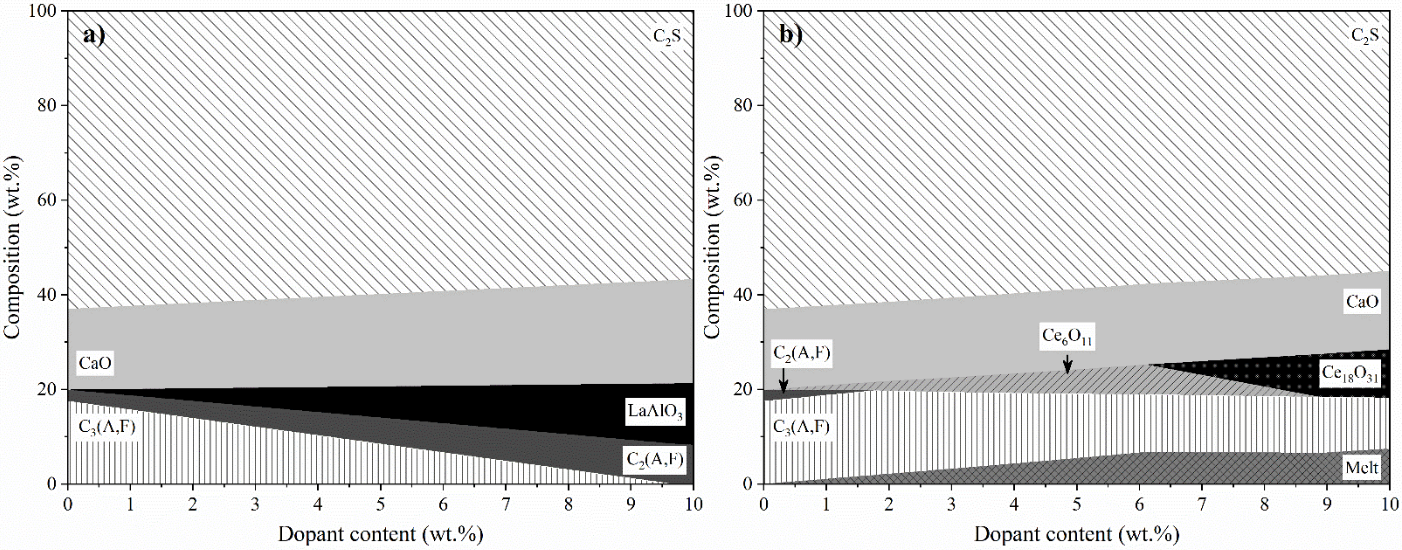

Fig. 1. Composition modelled for clinker produced at 1200 °C and doped with up to 10 wt.% lanthanum (a) and cerium (b) oxides.

Although the thermodynamic database includes the cerium aluminate perovskite [19], the simulations did not identify it (Fig. 1b). Previous studies have shown that the combining potential of Ce in structures containing aluminium depends on several factors, including processing in a reducing atmosphere, pressure of $O_2$ in the atmosphere, proportion of other impurities in the reagents, and heat treatment conditions [34]–[36]. Thermodynamic calculations showed $Ce_2O_3$ did not react with $Al_2O_3$ in the clinker raw meal, remaining in its pure crystalline forms and varying as the dopant content increased ($CeO_2$, $Ce_6O_{11}$, and $Ce_{18}O_{31}$). Additional experimental investigations are necessary to understand the Ce action mechanism during clinkering and the formation of new solid compounds containing this element.

### 3.3. Composition of lanthanide-doped clinkers at 1400 °C

The phase evolution at 1400 °C as a function of the dopant increment shows that La, Pr, Eu, Gd, and Nd enhanced $C_3S$ formation (Fig. 2a). Up to 3% dopant, the $C_3S$ content shows a positive development rate, starting from 76.3 wt.% (0% dopant) and reaching up to 79.0 wt.% (3% dopant). This behaviour is related to the $C_2S$ destabilisation, which starts from 3.4 wt.% and is depleted in this range (Fig. 2a). In this sense, lanthanides improve the clinker composition, increasing the $C_3S$ content by optimising the reaction between $C_2S$ and CaO dissolved in the melt phase. A similar effect was observed in experimental samples doped with Praseodymium (Pr) [37].

After 3 wt.% dopant, the $C_3S$ content decreased gradually, reaching 74.9 wt.% when 10 wt.% dopant was added. However, it is noteworthy that this percentage was improved, since the system produced 98% of the reference $C_3S$ amount (instead of 90%) even with 10 wt.% substitution of raw materials by lanthanides. In this range, the depletion of $C_2S$ limits the $C_3S$ growth. After 8 wt.% dopant, part of the melt phase recrystallised as $C_2(A,F)$. The results do not fully explain the recrystallisation occurring at high lanthanide contents. There are no lanthanides in the melt phase. Furthermore, resolidification occurs at different levels for each dopant, starting at 8.7 wt.% for $La_2O_3$, followed by $Pr_2O_3$ (8.8 wt.%), $Nd_2O_3$ (9.0 wt.%), and $Eu_2O_3$ (9.3 wt.%). In this sense, high levels of this oxides (8~10%) increased the melting point of the clinker raw meal, promoting a considerably lower content of the melt phase at 1400 °C.

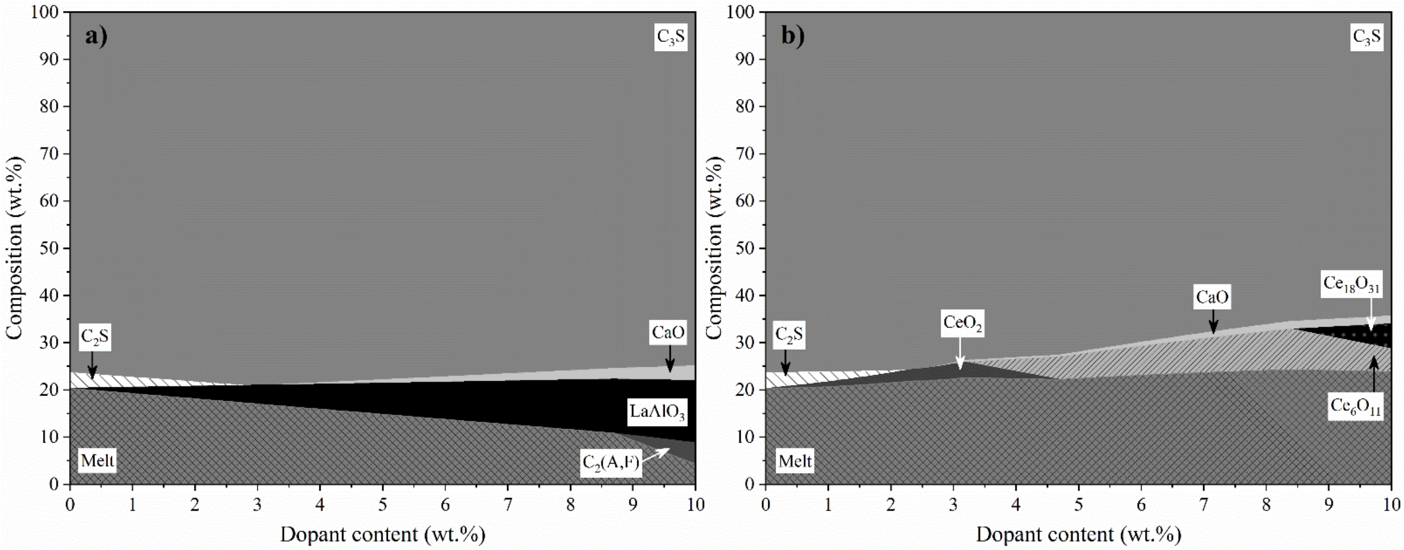

Fig. 2. Composition modelled for clinker produced at 1400 °C and doped with up to 10 wt.% lanthanum (a) and cerium (b) oxides.

Cerium promoted discrepant effects compared to the analysed lanthanides (Fig. 2b). Although the system started with the same $C_2S$ content (3.4 wt.%) and it was depleted in advance (occurring at 2.3 wt.% $Ce_2O_3$), the $C_3S$ content declined for increasing dopant levels. It reached 64.3 wt.% when 10 wt.% $Ce_2O_3$ was added, i.e., 84% of the calculated $C_3S$ for OPC (76.3 wt.%). This decrease may be related to the $SiO_2$ destabilisation. In this sense, $C_3S$ tends to decompose into solid CaO and molten $SiO_2$. The increased free CaO and melt in the $C_3S$ depletion regions evidenced this behaviour (Fig. 2b).

### 3.4. Emissions

Table 2 quantifies the emission of potentially polluting gases containing lanthanides accessed by thermodynamic modelling.

Table 2. Emission of compounds containing lanthanides simulated by thermodynamic modelling of the clinkering of raw meals containing 10 wt.% lanthanide oxide (1400 °C).

| Lanthanide | Compound | Emission (µg/t of clinker) |
|---|---|---|
| La | La | $5.7\ 10^{-22}$ |
| | $La_2$ | $9.8\ 10^{-48}$ |
| | LaO | $1.0\ 10^{-7}$ |
| | $La_2O$ | $8.1\ 10^{-31}$ |
| | $La_2O_2$ | $8.6\ 10^{-18}$ |
| Pr | Pr | $2.6\ 10^{-20}$ |
| | PrO | $1.7\ 10^{-6}$ |
| Eu | Eu | $2.6\ 10^{-12}$ |
| | EuO | $8.1\ 10^{-7}$ |
| | $Eu_2O$ | $1.4\ 10^{-22}$ |
| | $Eu_2O_2$ | $4.6\ 10^{-14}$ |
| Nd | Nd | $1.7\ 10^{-19}$ |
| | NdO | $1.1\ 10^{-7}$ |
| | $NdO_2$ | 43.16 |
| Gd | Gd | $5.8\ 10^{-21}$ |

All dopants showed negligible emission levels. Nd had the highest emission potential. However, the volatilised phase ($NdO_2$) was in the order of micrograms per ton of clinker produced, a value easily mitigated by the protection infrastructure of industrial kilns. On the other hand, the modelling did not detect the emission of gases containing Ce. This behaviour was attributed to the stability of its oxides as solid phases, as discussed in the previous section. For La, Pr, and Eu, the emission tended to higher values when the oxidation state of these elements was $2^+$. According to the modelling, the emission of polluting gases containing lanthanides does not promote environmental risk since the emissions were approximately zero even when co-processing 10 wt.% of lanthanide oxide in the clinker raw meal.

## 4. Conclusions

According to the results of this study, the following conclusions can be drawn:

La, Pr, Eu, and Nd showed similar effects, enhancing the $C_3S$ content. This effect occurred on a larger scale for up to 3 wt.% of added dopant, when $C_2S$ is depleted in the clinker. Ce promoted notably different behaviours on phase assemblage, decreasing the $C_3S$ development depending on the dopant content.

Increasing lanthanide content generally stabilised $C_2(A,F)$ rather than $C_3(A,F)$, suggesting that these elements may be applicable to produce high-ferrite and sulphate-resistant cements.

Co-processing lanthanides promoted the formation of new compounds, mainly the cubic perovskite containing Al and O ($LaAlO_3$, $NdAlO_3$, $PrAlO_3$, $EuAlO_3$, and $GdAlO_3$), with increasing values as the dopant content is increased. However, $Ce_2O_3$ remained in its pure crystalline forms, varying as the dopant content increased ($CeO_2$, $Ce_6O_{11}$, and $Ce_{18}O_{31}$).

The emission of polluting gases containing lanthanides was low even when co-processing 10 wt.% of lanthanide oxide in the clinker raw meal. However, it needs to be compared with the limits of the environmental regulations of each location. Furthermore, investigations are needed to understand how impurities could be immobilised in the cementitious material.

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