

## UTILISATION OF CEMENT KILN DUST FOR THE ACTIVATION OF FLY ASH IN LOW STRENGTH APPLICATIONS

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## Abstract

Cement kiln dust (CKD) is a by-product of the cement manufacturing process, the composition of which can vary widely. Recent years of using alternative fuels have resulted in higher chloride and alkali contents within CKDs; as such, this limits the applications in which CKDs can be utilised. Due to the high alkalinity of CKDs, they can potentially be utilised in the activation of pulverized fuel ash (PFA) for low strength un-reinforced applications. The potential reactivity of a CKD can be estimated from its composition; mainly, that which contains higher free-lime content will be more reactive than that containing higher unreactive calcium carbonate content. This study focuses on the hydration kinetics and mechanical properties of a CKD with 29.5% free lime blended in various proportions with PFA and Portland cement. Paste samples using a water to binder ratio of 0.35 were cast in 40 x 40 x 160 mm moulds, and the resulting compressive strengths measured at 28 and 56 days. The hydration products at 56 days were investigated by X-ray diffraction and thermogravimetric analysis. The results show that the CKD, containing high free-lime content, has the potential to activate PFA and provide sufficient mechanical properties for low strength applications.

## Keywords:

Cement kiln dust (CKD); Pulverised fuel ash (PFA); Compressive strength; X-ray diffraction (XRD); Thermogravimetric analysis (TGA).

## **1 INTRODUCTION**

Cement kiln dust (CKD) is a by-product of the Portland cement manufacturing process, produced during the thermal processing of raw materials and fuels. Due to the generation of large quantities, it is important from both an environmental and economic view to find suitable applications for this material. While some of the material can be returned into the manufacturing process as a raw material, the high contents of alkalis, sulfates and chlorides become a limiting factor. Moreover, in recent years, the burning of alternative fuels such as solid recovered fuel (SRF) has to lead to an increase in the alkali and chloride content in the produced CKD.

Alternatively, CKD can potentially be used as an additive to cement blends which contain alkali activated materials such as fly ash or slag. In these cases, the Portland cement provides high early strength, while the alkalis from the CKD can activate the fly ash or slag and improve the long term strength and durability of the concrete. With additions of up to 10 - 15 % CKD by weight to high volume fly ash/slag concretes, similar or improved strengths were achieved to blend with no added CKD [Bondar 2014, Sadique 2016].

However, there are a number of drawbacks limiting the use of CKD in reinforced concrete applications. Firstly, the high chloride content of CKD presents a high risk for corrosion of the steel reinforcement. Moreover, the high alkali content can potentially cause alkali-silica reactions (ASR) between the pore fluid of the cement and the aggregates within the concrete, which can lead to expansion and cracking of the concrete.

Therefore, alternatives need to be investigated for the use of CKD where the chloride and alkali contents do not present any durability problems. The potential for this lies in the utilization of the high alkali content to activate fly ash or slag, in non-reinforced low strength applications.

Although it has previously been observed that CKD could not activate the reaction of fly ash and slags with no cement added, this was attributed this to the high calcium carbonate (CaCO<sub>3</sub>) content of 52% in the CKD used [Peyronnard 2011]. However, it was acknowledged that this finding cannot be generalized due to the highly variable composition of CKD. The composition of CKDs depends on many variables such as the raw materials used for the cement production, the type of kiln, and the type of fuel used. Due to this, wide variations are observed in the composition of CKDs between various plants, and can even be found

to vary within the one plant when characterized at different times.

When blended with fly and cement, the high alkalinity provided by CKD can result in enhanced compressive strength as a result of the increased pozzolanic activation of the fly ash [Dyer 1991]. This activation has been found to result in the formation of calcium-aluminate-hydrates (C-A-H) and calcium-silicate-hydrates (C-S-H) which can contribute to strength gain [Buchwald 2005].

While most CKDs tend to generate relatively high pH levels when mixed with water, enabling them to potentially activate the pozzolanic reaction of fly ash, the importance of the free-lime content must be emphasized when determining the reactivity of a CKD [Peethamparan 2008]. It has been identified that the reactivity of CKD containing high free-lime (free-CaO) and calcium hydroxide (Ca(OH)<sub>2</sub>) was higher than that containing CaCO<sub>3</sub> [Buchwald 2005]. CaCO<sub>3</sub> is essentially inert and its contribution would be as a filler material with no reactivity potential.

The present study focuses on the compressive strength of a CKD blended in various proportions with pulverized fuel ash (PFA) and Portland cement for low strength applications. Hydration products were also assessed to aid in the understanding of the PFA activation potential of the CKD.

## 2 MATERIALS AND METHODS

## 2.1 Materials

The chemical and oxide compositions of the CKD, PFA (class F), and CEM I used are shown in Tab. 1. The CKD used was obtained from a cement plant where SRF is used as an alternative fuel, which resulted in a high chloride content of 11.68%. Tab. 2 shows mineralogical composition of the CKD, as characterised by quantitative X-Ray Diffraction (XRD) Rietveld analysis. Containing 29.5% free-lime, and no CaCO<sub>3</sub>, the CKD shows potential for activation of the PFA.

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Constituent	CKD (%)	PFA (%)	CEM I (%)
CO <sub>2</sub>	1.27	5.40	
Water	1.06		
LOI	2.33	5.40	3.00
SiO <sub>2</sub>	8.16	51.77	19.83
Al <sub>2</sub> O <sub>3</sub>	3.68	21.54	4.80
TiO <sub>2</sub>	0.12	0.94	
P <sub>2</sub> O <sub>5</sub>	0.12	0.68	
Fe <sub>2</sub> O <sub>3</sub>	1.62	6.28	3.02
MgO	1.46	2.06	
CaO	47.98	5.53	63.06
SO₃	7.04	0.84	2.48
Na <sub>2</sub> O	3.62	2.55	
K <sub>2</sub> O	14.64	2.40	
CI-	11.68		

Tab. 1: Oxide composition of materials

The main crystalline phases of the PFA were identified to be quartz and mullite, both of which are considered unreactive. The reactivity potential of the PFA lies within the amorphous portion, which is likely to be composed mainly of aluminosilicate glasses. As quantified by XRD-Rietveld using the external G-factor method [Jansen 2011], the amorphous content of the PFA was found to be 73.9%. In order to ensure consistency between samples, the PFA was dried at 105°C prior to use.

The mix designs used are shown in Tab. 3, ranging samples containing various amounts of CKD, PFA, and CEM I. All samples were cast using a water to binder (w/b) ratio of 0.35, as this was visually observed to produce good workability without bleeding occurring.

Tab. 2: Mineralogical composition of CKD

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Mineralogical phase	Chemical composition	Phase content (%)
Free lime	CaO	29.5
Sylvite	KCI	21.4
Belite	Ca <sub>2</sub> SiO <sub>4</sub>	17.5
Dolomite	CaMg(CO <sub>3</sub> ) <sub>2</sub>	6.0
Portlandite	Ca(OH) <sub>2</sub>	3.8
Anhydrite	CaSO <sub>4</sub>	3.7
Arcanite	K <sub>2</sub> SO <sub>4</sub>	8.4
Ferrite	Ca <sub>2</sub> (Al,Fe) <sub>2</sub> O <sub>5</sub>	5.2
Quartz	SiO <sub>2</sub>	3.1
Syngenite	K₂Ca(SO₄)₂·H₂O	1.3

Tab. 3: Mix designs and proportions

Mix Design	CKD (%)	PFA (%)	CEM I (%)
10-90P	10	90	
20-80P	20	80	
30-70P	30	70	
40-60P	40	60	
50-50P	50	50	
40-60P-5C	38	60	2
50-50P-5C	47.5	50	2.5
40-60P-10C	36	60	4
50-50P-10C	45	50	5

## 2.2 Methods

#### Compressive strength

The CKD and PFA were pre-blended prior to adding the mixing water and mechanically mixing for 3 minutes. The pastes were then cast and vibrated into prisms of 40 x 40 x 160 mm, and demoulded after 48 hours; at 24 hours, samples were observed to be too weak for demoulding. Further to this, samples were cured either in air or in a water bath, both which were controlled at 20°C. After the specified curing time of either 28 or 56 days, the prisms were tested for compressive strength following the standard method in BS EN 196-1. Average values for compressive strength values are based on four replicate samples.

## Characterisation of hydrates

The hydrated pastes were characterised using samples prepared with distilled water, which were cast and cured in 50 mL sealed bottles. At 56 days, the samples were ground to a powder, and tested immediately without ceasing hydration to prevent any damage to crystalline structures.

#### X-Ray Diffraction (XRD)

XRD data were collected using a PANAlytical XPert Powder diffractometer in the Bragg-Brentano geometry

with tube operating conditions of 45 kV and 40mA, soller slits of 0.04 rad, and CuK $\alpha$  radiation with a beam wavelength of 1.5418 Å. Patterns were measured from 5° to 65° 20, with a step size of 0.0164° and time per step of 0.5 s, resulting in 30 minute scans. Rietveld refinements were carried out using HighScore Plus software.

#### Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) was carried out on a TG 209 F1 Libra using ~40 mg of sample in a flowing nitrogen atmosphere from  $20^{\circ}$ C to  $950^{\circ}$ C, and a heating rate of  $20^{\circ}$ C/min. Derivative thermogravimetric analysis (DTG) was used to identify the presence of any amorphous phases.

## **3 RESULTS AND DISCUSSION**

#### 3.1 Compressive strength

The average measured compressive strengths of the mixes containing CKD and PFA only at 28 and 56 days are shown in Fig. 1. No strength was recorded for samples with the lowest addition of CKD to PFA (sample 10-90P), which was likely due to insufficient alkalinity to activate any reaction of the PFA. Upon increasing the CKD content, the strength was likewise observed to increase with a maximum strength achieved by mix 40-60P of 13.9 MPa and 17.7 MPa at 28 and 56 days respectively. Increasing the CKD content further resulted in a reduction of the strength, suggesting that the optimum CKD for activation of the PFA had been exceeded.



#### **Mix Design**

# Fig. 1: Compressive strength of CKD-PFA paste prisms at 28 and 56 days.

Fig. 2 shows the average compressive strength of the CKD-PFA-CEM blends at 28 and 56 days. The addition of small amounts of cement in these blends resulted in higher strengths being achieved in all cases, with a maximum strength of 21.4 MPa for mix 40-60P-10C.

All samples were observed to have moderately increased in strength between 28 and 56 days. The pozzolanic reaction of PFA tends to be a much slower process than the hydration of cement, and will continue to react beyond 28 days. However, only a minor increase in strength was observed for sample 20-80P between 28 and 56 days as the pozzolanic reaction of the PFA would be low due to low activation.



#### Mix Design

# Fig. 2: Compressive strength of CKD-PFA-CEM paste prisms at 28 and 56 days.

Curing of samples in water displayed a negative effect on the properties of the material; Fig. 3 shows an example of the expansion and deformation of a sample cured in water. These samples either produced very low strengths in comparison with air cured samples, or no strength was recorded due to heavy expansion and weakening of material. This is similar to the behaviour reported for various other alkali-activated materials, which were observed to have deteriorated strengths upon water curing in comparison with air [Kirschner 2004, Zuhua 2009, Al-Shather 2016].



Fig. 3: Expansion and deformation of a CKD – PFA paste prism cured in water for 56 days.

#### 3.2 Hydration products

The hydration products were investigated on four of the mix designs at 56 days, with the XRD patterns shown in Fig. 4. The broad "hump" between ~15° and ~35° 20 associated with the amorphous content is most apparent in the 20-80P mix, and appears to reduce with increasing CKD content. This is likely the result of two factors: (i) the reduction in PFA content reduces the initial amorphous content of the mix, and (ii) increasing the CKD content provides conditions for higher activation and reactivity of the PFA.

At 56 days, the free-lime contained within the CKD was fully consumed in all cases. Upon initial contact with the mixing water, the free-lime is rapidly converted to calcium hydroxide (portlandite). Increasing the CKD content results in higher calcium hydroxide formation and higher alkalinity of the pore solution; this provides suitable conditions for the pozzolanic reaction with the aluminosilicate glasses in the PFA to form C-S-H phases. Compressive strength results were in agreement with this, whereby higher strengths were achieved at the higher CKD containing samples. However, the XRD patterns show that the amount of residual calcium hydroxide at 56 days increases as the CKD content increases. This suggests that the calcium hydroxide is in excess of the amount required to react with the PFA at 56 days. It is possible that the pozzolanic reaction of the PFA will continue to progress slowly with further curing time. On the other hand, the reduction in strength with addition of CKD beyond 40% suggests rather that the optimum CKD for reaction with the PFA has been surpassed; it is likely that the total pozzolanic reaction is close to its full potential.



Fig. 4: XRD patterns of hydrated CKD-PFA paste blends at 56 days, where E = ettringite, Hc = hemicarboaluminate, M = mullite, P = portlandite (calcium hydroxide), Q = quartz, S = sylvite, and Cc = calcium carbonate.

Unreactive quartz and mullite remained present in all samples at 56 days. While sylvite was almost completely absent from the samples containing only 20 and 30% CKD, the residual sylvite content at 56 days increased with further CKD addition. At the lower CKD contents, uptake of the small amounts of potassium and chloride ions present into the C-S-H structure may have been possible.

The main crystalline product of CKD-PFA blends has been previously been observed to be ettringite [Wang 2004], which was also formed in all samples in the present study. Ettringite formation occurs due to reaction of the sulfate bearing phases, anhydrite and arcanite, with the alumina from ferrite or the PFA. Ettringite is known to contribute to strength gain as it has a lower density (1.78 g cm<sup>-3</sup>) than many other hydrates in cements, and is suggested to have good space filling properties due to the dense packing of its characteristic needle-like crystals [Glasser 2001].

In addition to this, XRD showed the precipitation of hemi-carboaluminate and calcium carbonate in all samples, the carbonate being provided from the PFA.

The TGA-DTG results, shown in Fig. 5, confirmed the presence of ettringite and calcium hydroxide, in addition to the formation of amorphous aluminium hydroxide (AH<sub>3</sub>) gel. As the CKD content in the binder increased, the aluminium hydroxide gel was observed to increase due to increased dissolution of the aluminosilicates in the PFA.

The presence of C-S-H could not be directly identified in the DTG plots as the dehydration of this phase typically occurs within the same range of temperatures as ettringite and continues to loss mass across a wide range of temperatures. However, the floating baseline in the DTG plot, and the lack of any crystalline silicate bearing phases in the XRD patterns, suggested that amorphous C-S-H had formed.



Fig. 5: TGA-DTG plots of hydrated CKD-PFA paste blends at 56 day.

## **4** CONCLUSIONS

The present study showed that CKD, containing high free-lime content, has the potential to activate the pozzolanic reaction of PFA and provide sufficient mechanical properties for low strength applications. The main hydration products were identified to be ettringite, calcium carbonate, hemi-carboaluminate, portlandite, and amorphous C-S-H and aluminium hydroxide. It was found that the optimum mix ratio for maximum compressive strength was 40% CKD and 60% PFA, where the calcium hydroxide formed was sufficient to activate the PFA. Beyond this point, residual calcium hydroxide persisted, and the compressive strength was reduced. Further work will aim to investigate the microstructure of the hydrated pastes, and to quantify the hydrates formed over time in order to understand the hydration kinetics of these binders.

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