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Pyro processing cement kiln bypass dust: enhancing clinker phase formation

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Abstract

The valorisation of cement kiln bypass dust (CBPD) is explored for sustainable production of cementitious clinker phases. CBPD can replace the calcareous component in cement manufacture and allow for a reduction in CO_2 emissions as the calcium component in CBPD is mostly decarbonised. CBPD was heated with/out the addition of alumina or silica at temperatures of 900 – 1100°C to produce clinker phases. Belite and mayenite formed at temperatures as low as 900°C, while alite formation was achieved at 1200°C, which is significantly lower than is conventional (~1450°C). Alite is thermodynamically stable only above 1250°C; thus, the reduced temperature is potentially owing to the presence of chloride found in the CBPD (as KCl) which was also eventually simultaneously removed through pyro processing at 1100 – 1200°C. The investigation also confirmed that the formation of belite is enhanced in the presence of molten KCl.

Keywords: Cement kiln bypass dust; cement manufacture; clinker; pyro processing; waste valorisation; low-carbon clinker

1. Introduction and background

The cement industry is generating and emitting significant quantities of carbon dioxide (CO_2) that amounts to approx. 8% of global man-made emissions [1]. In Portland cement (PC) manufacture, approximately 90 % of the CO_2 emissions are direct emissions from the burning of fossil fuels (~30%) and the decomposition of calcium carbonate (~60%), mainly from limestone, with the remaining ~10% being indirect emissions such as electricity consumption [2]. The burning of the fuels is necessary to reach a temperature of approximately 1450°C, for clinkering.

Modern manufacture of PC utilises the preheater rotary kiln configuration. To avoid damage in subsequent concrete, cement clinker is designed to meet the low-alkali and chlorine specifications; thus, a bypass is used to extract the dust containing air which includes alkali, sulphates, and chlorides that originated from the kiln raw meal or fuel. The bypass also helps break the volatilisation cycle within the process and avoid kiln operational problems. The bypass is positioned between the kiln inlet and the preheater to extract dust-containing air, where temperatures exceed 900°C; thus, the calcareous component in the collected dust will be mostly decarbonised. The removed solids/dust is called cement kiln bypass dust (CBPD), and the amount of this dust produced is approximately 2% of clinker production by weight. Global cement production of 4.1 billion tonnes in 2017 [3] equates to a substantial amount of bypass dust being generated. It should be noted that not all kilns are equipped with a bypass and kilns with a bypass system are more frequent in Europe, and to some extent the USA, than in other regions. CBPD is often classified as cement kiln dust (CKD); but, the two are not

the same and should be differentiated. CBPD is collected from the bypass only while CKD can be collected from the flue gas leaving the preheater tower at lower temperatures and is produced in larger quantities (15 – 20 times) than CBPD. CKD will contain calcium carbonate and less chloride and unlike CBPD, CKD is generally recycled during cement manufacture either as raw meal or blended with the final cement while CBPD is not.

CBPD is usually unexploited and landfilled at a monetary and environmental cost. The recycling of CBPD Is interesting due to its the negative effects on human health and ecotoxicity [4, 5]. Research on the valorisation of CBPD has focused on using it as an additive to cement [6], for backfilling excavations [7], for sand and soil stabilization [8, 9], to activate slags in cement blends [10], for the manufacture of vitrified sewer pipes [11]; or, thermally treated along with other material to produce glass/ceramic for sustainable disposal [12] or pozzolanic cementitious material [13]. The production of cement clinker from CBPD has not been previously studied and will be explored in this work.

CBPD is mainly composed of calcium oxide (CaO), which is the key component in traditional cement clinker. Differing from the limestone used for the conventional clinker production, the calcium component in the CBPD is already in the de-carbonised form; thus, producing cement from this material can allow for the reduction in the raw-material derived carbon emissions. Additionally, CBPD contains salts (such as KCl) that will melt at temperatures approaching clinkering conditions. These salts can act as a flux to improve the extent of reactions [14] and can be used to reduce the temperature required for cement manufacture [15-17]; thus, enabling a reduction in fuel-derived CO_2 emissions.

Cement production is on the rise and with it, the production of CBPD. Further utilisation of CBPD is therefore advantageous in order to minimise its negative influence over the environment and the cost of landfilling. The aim of the title study is to explore the pyro processing of CBPD with/out additives for potential manufacture of low-carbon cement clinker or supplementary cementitious material, and at reduced temperatures than conventional; thus, extending the reusability of the by-product in the conventional cement production process and promoting green and circular solutions in the cement industry.

2. Objectives

This work seeks to assess the valorisation of CBPD through the pyro processing/calcination of CBPD with/out the addition of alumina and silica in order to understand the influence of the intrinsic minor components on clinkering. Components within the CBPD can enhance the formation of cementitious clinker phases at a lower temperature than is conventional, by acting as a flux/mineraliser or through entropy stabilisation due to ionic substitution in clinker phases. The thermal treatment will also be used to burn off the undesirable salts within the mix. CBPD and blends with SiO_2 and/or Al_2O_3 are heated at 900 – 1200°C and the phases formed are presented. Reagent grade Al_2O_3 and SiO_2, are used as surrogates for clays to demonstrate separately the formation of silicate and aluminate phases. For application, aluminosilicate sources will need to be added to the raw-mix before firing in order to avoid the persistence of free CaO. To elucidate the role of minor components/impurities, the minor components found in CBPD and in similar quantities are blended individually with reagent grade raw materials to produce a “simplified CBPD” before firing.

3. Materials and methods

3.1. Clinker phase notation

The cement oxide notation used in this work is: C = CaO, S = SiO_2, A = Al_2O_3, and F = Fe_2O_3. Major clinker phases are presented as alite (C_3S), belite (C_2S), ferrite, ($C_2(A_xF_{1-x})$ where 0< x <1), and mayenite ($C_{12}A_7$); although these phases may have incorporated other minor elements, this was not examined in the course of this work. All belite reported in this work was detected as the larnite (beta) polymorph and no other polymorphs of belite were detected.

3.2. Materials

Cement kiln bypass dust (CBPD) used in the title study was provided by CEMEX Asia Research AG and originated from an EU cement plant. To remove the moisture content in the powder, the CBPD was dried overnight in an oven at ~80°C prior to the detailed characterisation and successive experimental work. The following reagent grade materials: Al_2O_3, $CaCO_3$, Fe_2O_3, MgO, $CaSO_4.2H_2O$, SiO_2 (quartz), and KCl were also used in the present study as additives. Details on the reagent grade chemicals are provided in Table 1.

Table 1: Details of the reagent grade chemicals used in this work.

	SiO_2	**Al_2O_3**	**$CaCO_3$**	**Fe_2O_3**	**MgO**	**$CaSO_4.2H_2O$**	**KCl**
Purity	≥95%	99%	99%	≥95%	98%	≥98%	≥99%
Supplier	Sigma-Aldrich	Acros Organics	Acros Organics	Fisher Scientific	Acros Organics	Acros Organics	Sigma-Aldrich
Code	83340-1kg	21570010	450680010	I/1013/60	205150025	225275000	P9333-500G

3.3. Methods used to characterise CBPD and pyro processed samples

X-ray diffraction (XRD) was used throughout the present investigation to identify the phases in the raw CBPD and pyro processed samples. A Bruker D2 PHASER was used on powdered materials with a Cu-Kα radiation source operating at 30kV and 10mA. For the measurements, the 1 mm primary divergence slit was used with the 3 mm air scatter screen module. X-ray patterns were collected in the range of 5 – 70° 2θ at 0.02° increments and 0.5 s per step. The lower and upper discriminator settings were set to 0.11 V and 0.25 V respectively and samples were rotated at 15 rpm. The collected diffraction patterns were assessed using the DIFFRAC.SUITE EVA software furnished with the PDF-4 2019 database.

X-Ray Fluorescence (XRF) was used to determine chemical composition of the dried CBPD. The measurement was conducted using a PANalytical Zetium instrument and the PANalytical Omnian package was used to determine the elemental concentrations in weight %. The 40 mm beads were prepared for the measurements using a Claisse LeNeo Fluxer by mixing 1 g of sample with 10 g of lithium tetraborate salt (with 0.5% LiI). The mixture was fused through heating in 5 steps before being poured and cooled: 1) 4 min at 1065°C, 2) 3 min at 1065°C rocking at 10 rpm and an angle of 15°, 3) 6 min at 1065°C rocking at 30 rpm and an angle of 40°, 4) 1 min at 1000°C, and 5) 4 min at 1000°C rocking at 25 rpm and an angle of 45°.

Inductively coupled plasma – optical emission spectrometry (ICP-OES) was also used to support the compositional analysis of the CBPD. A Spectro-Ciros-Vision optical emission spectrometer was used for the measurement. Two or more emission lines were used to determine the elements and eliminating the risk of spectral overlap interferences. Calibration

was conducted using multi-element standards of known concentrations from certified stock solutions. Samples were prepared by dissolving 0.125 g of CBPD in 5 mL of concentrated HNO_3 in a glass tube, placed into the heating block and the temperature gradually raised to 150°C and maintained for 15 minutes. After cooling, the solution was diluted to 50 mL. A 20-fold dilution was then measured. Samples were also prepared using a combination of aqua regia and HF, or a combination of HNO_3 and HF. Either 0.0625 g or 0.03125 g of CBPD was mixed with 12 mL of aqua regia or 5 mL of HNO_3 in a PTFE tube, heated at 150°C for 30 minutes; 1 mL of HF was then carefully added, and the samples were allowed to reflux for 10 minutes. Then, 1 mL HNO_3 or 2 mL aqua regia as well as 1 ml HF was added and left for a further 10 minutes. Solutions were immediately transferred to a larger tube to make up to 50 mL with 1 % nitric acid. Samples were shaken and analysis of 20-fold and 600-fold dilutions with 1 % nitric acid was immediately carried out; the 600-fold dilution was used to analyse the bulk elements and the 20-fold dilution was used to measure minor elements.

Simultaneous thermal analyses through thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were also conducted on the dried CBPD in order to explore its behaviour at various temperatures. Measurements were made on approximately 30 mg of sample in an alumina pan using a TA Instruments SDT Q600 operating from 20 – 1400°C with a heating rate of 10 °C/min under 100 mL/min flowing nitrogen gas.

3.4. Pyro processing CBPD

Pyro processing of CBPD was first investigated without any additives, i.e., the CBPD was subjected to high temperatures. The CBPD samples were prepared in the form of powder (3

g per sample) and pellet (1.5 g × 2 pellets per sample). Pellets were made using a hydraulic press with a mould diameter of 2 cm and applying pressure of 64 MPa for one minute. The pellet-pressing from powder was conducted without the addition of any liquid. The samples were placed in 30 mL alumina crucibles and introduced into a muffle furnace preheated in air at three different temperatures: 900°C, 1100°C, or 1200°C. The minimum heating temperature of 900°C was selected to allow for the melting of the potassium chloride present in the CBPD and with an aim of providing a flux. Three heating times studied were: 30, 60, and 120 minutes both for the powder and pressed samples. Considering the drop in the furnace temperature by approximately 50°C when introducing the samples, the initial 10 minutes were discarded from the heating time (30, 60, or 120 mins); this allowed for the furnace temperature to return to the temperature targeted. After the designated heating times, samples were directly removed from the furnace still at the target temperatures and cooled in air at ambient conditions. Samples were then weighed and ground using a mortar and a pestle for further analyses.

3.5. Interaction of CBPD with additives

Experiments were conducted to test the formation of targeted cement clinker phases (alite, belite, and mayenite) with the addition of SiO_2 and Al_2O_3. These experiments were conducted also to assess the effectiveness of salt content as a flux to obtain enhanced reaction to clinker phases at reduced temperatures. The amount of SiO_2, Al_2O_3 and CBPD was calculated to generate a total sample weight of 3 g based on the XRF data (shown in the result section), if all CaO content would react to form the desired target phase.

The processing temperatures and the composition of the samples are provided in Table 2. After addition of reagents to CBPD, the samples were homogenised with a mortar and a pestle and placed in cylindrical alumina crucibles in powder form. The samples were then placed in a muffle furnace preheated at 1100°C (for belite and mayenite) and 1200°C (for alite) to thermally treat in air for 30, 60, and 120 minutes. The samples, directly removed from the furnace still at the clinkering temperature and allowed to cool in air, were then ground with a mortar and a pestle.

Table 2: Heating temperatures and amounts of SiO_2 and Al_2O_3 added to CBPD to produce specific clinker phases. All three sets were each heated for 30, 60, and 120 mins.

Sample name	Target phase	Heating temperature (°C)	CBPD (g)	SiO_2 (g)	Al_2O_3 (g)
C_3S	Alite	1200	2.87	0.13	-
C_2S	Belite	1100	2.61	0.39	-
$C_{12}A_7$	Mayenite	1100	1.91	-	1.09

Cement phases are annotated using cement oxide notation: C = CaO, S = SiO_2, A = Al_2O_3.

3.6. Behaviour of simplified CBPD

In order to further investigate the effect of KCl and other constituents in the CBPD seperately, six "simplified CBPD" compositions (S-CBPD 1 – 6) were prepared using $CaCO_3$ and SiO_2 (stoichiometric to produce alite) with another constituent. The constituents considered are those with a significant composition (> 1 wt.%) in CBPD and the batch compositions of S-CBPD 1 – 6 are provided in Table 3. The weight percentage of elements was based on their composition in the as-received CBPD. Calcium carbonate was generally used as a source of CaO, but its amount was slightly reduced when calcium sulfate dihydrate was used as a source of SO_3, since it will also provide CaO. The required chemicals were mixed and homogenised through grinsding/mixing with a mortar and pestle for 10 minutes and placed into cylindrical alumina crucibles. The prepared samples were introduced into a muffle furnace preheated at

1200°C to thermally treat in air for 30 minutes. The heated samples were directly taken out from the furnace still at target temperature and ground with a mortar and pestle after cooling in air.

Table 3: Quantities of chemicals used in the simulated CBPD samples.

Sample	$CaCO_3$ (g)	SiO_2 (g)	Constituent of interest (g)
S-CBPD 1	2.59	0.41	-
S-CBPD 2	2.24	0.35	KCl (0.41)
S-CBPD 3	2.51	0.39	Al_2O_3 (0.10)
S-CBPD 4	2.54	0.40	Fe_2O_3 (0.06)
S-CBPD 5	2.52	0.40	MgO (0.08)
S-CBPD 6	2.44	0.41	$Ca_2SO_4.2H_2O$ (0.15)

4. Results and Discussion

4.1. Characteristics of CBPD

The XRD results of CBPD reveals it is composed of CaO, KCl, SiO_2, and $Ca(OH)_2$ as major phases; the presence of belite and ferrite is also detected. The annotated XRD diffroctogram of the raw CBPD is provided in Fig. 1. Table 4 shows the elemental composition of the CBPD obtained through XRF and ICP-OES analyses where constituents less than 0.1 wt.% are not included; two methods were used because sample preparation for XRF required processing at high temperatures, which could raise doubts due to the potential of KCl volatilization. The XRF and ICP analyses are in good agreement. If all Ca exists as oxide, more than 50 wt.% of CBPD is composed of CaO. If all the chlorine found in the XRF analysis is assumed to be bound to potassium as KCl as observed in the XRD data, this corresponds to 12.1 wt.% of KCl in the CBPD.

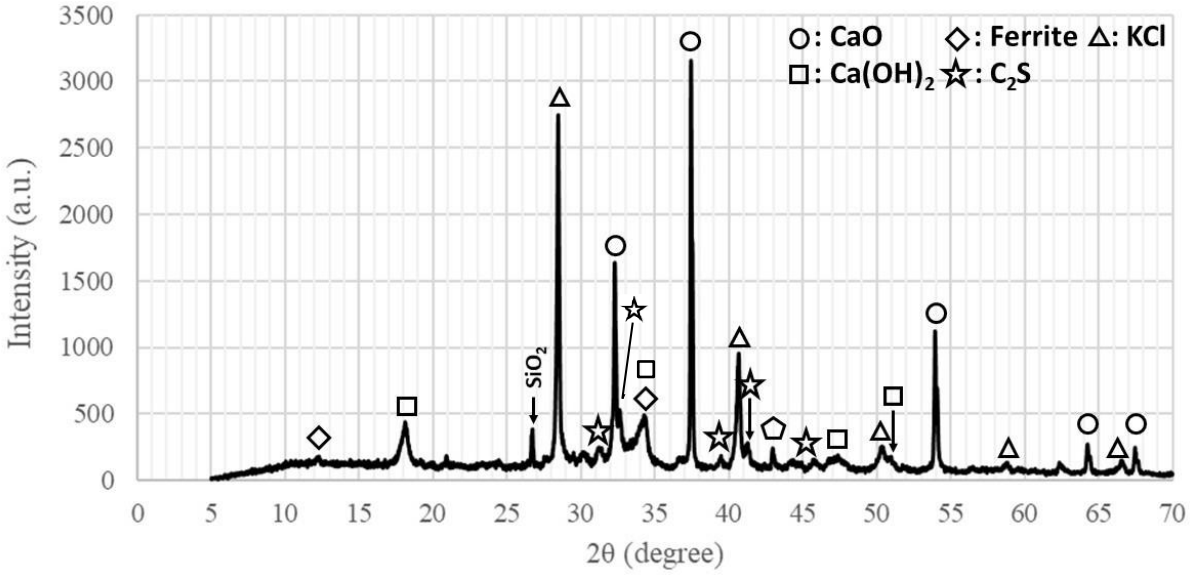


Figure 1: X-ray diffraction pattern of the raw cement kiln bypass dust (CBPD).

Table 4: Elemental composition (weight %) of cement kiln bypass dust obtained through both XRF and ICP-OES.

	Ca	Si	Cl	Al	K	Mg	S	Fe	Na	Br	I	Pb	Ti
XRF	38.0	6.9	5.8	2.1	9.4	1.7	0.9	1.6	0.4	0.5	0.3	0.16	0.1
ICP	35.8	6.7	-	1.4	8.6	1.5	0.9	1.5	0.4	-	-	0.13	0.1

Constituents less than 0.1 wt.% are not included
The ICP data for Si is from the samples dissolved in aqua regia/HF
The ICP data for Al, Fe, and Ti are taken from samples dissolved in HNO_3/HF
The ICP data for remaining elements are from samples dissolved in HNO_3 alone

A series of endothermic reactions are observed when CBPD is subjected to heating up to 1400°C as shown in the DSC data in Fig. 2; most of these events are associated with a weight loss as observed in the TG data in Fig. 3. The weight loss at ~390°C can be attributed to the decomposition of $Ca(OH)_2$ identified in XRD. The DSC peak at 573°C can be attributed to the inversion of α-quartz to β-quartz. The weight loss over 500 – 1000°C may be attributed to the possible melting and subsequent vaporisation of alkali and/or alkaline earth salts. For instance, the melting temperature of KCl is 770°C [18], and thus KCl can evaporate in this temperature range. The amount of KCl estimated by XRF was 12.1 wt.%, which seems to form the majority of the weight loss observed in this temperature region in the TG data. The weight

loss above 1000°C is likely the evaporation of sulfate salts (e.g. K_2SO_4 or $MgSO_4$) as a significant amount of sulfur was identified in the XRF data.

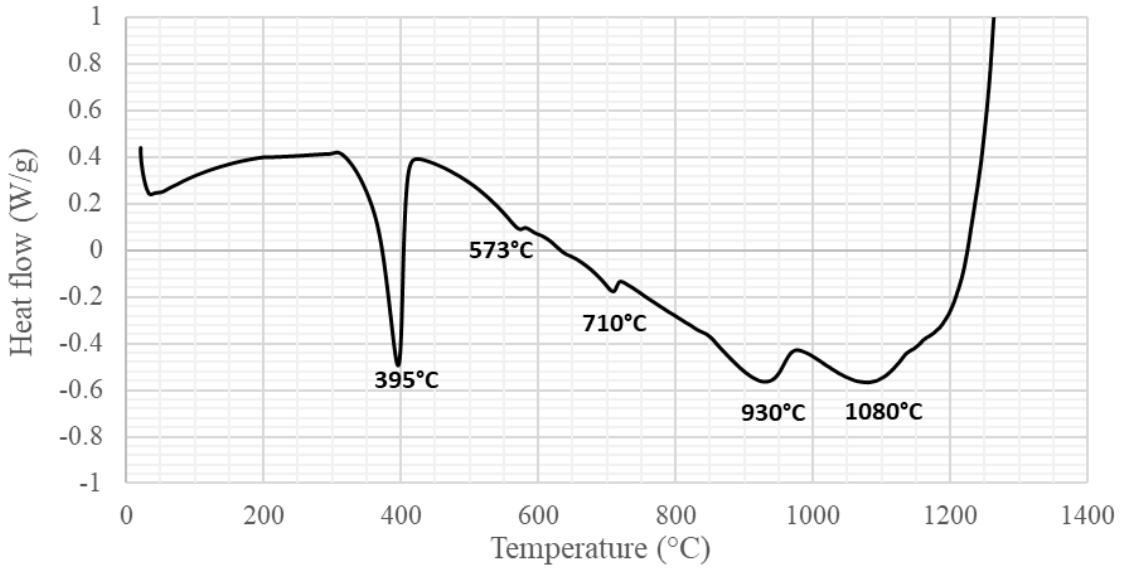


Figure 2: Differential scanning calorimetry analysis of cement kiln bypass dust.

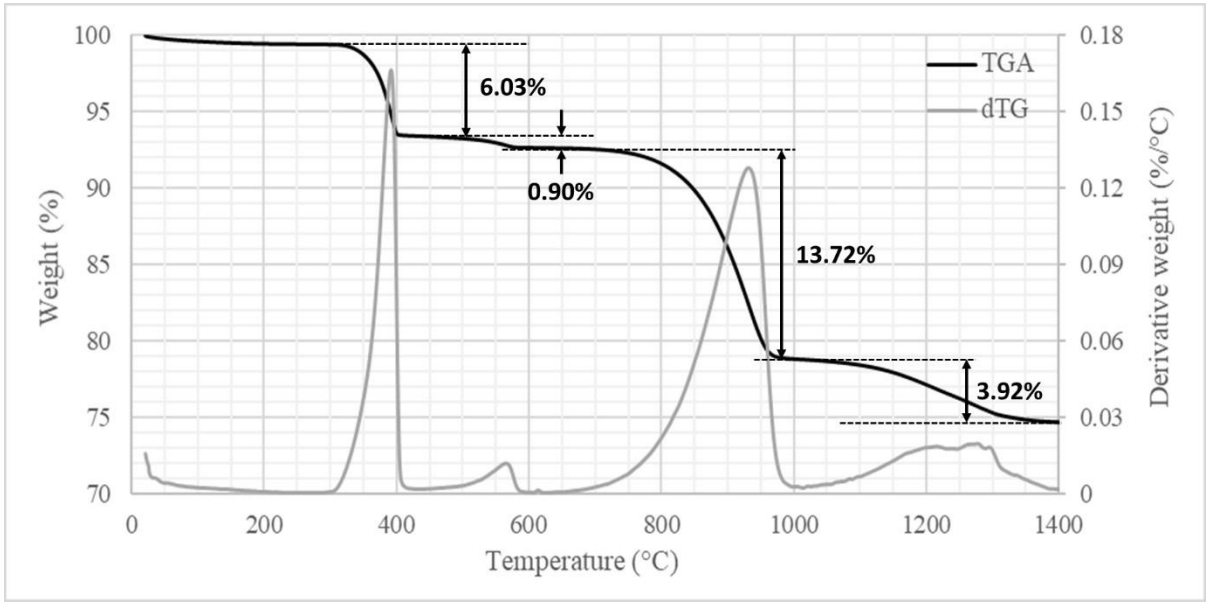


Figure 3: TGA (black) and differential thermogravimetric (DTG) (grey) analysis of CBPD.

4.2. Pyro processing CBPD: results

Table 5 summarises the phase composition of the heated samples determined from qualitative XRD analyses; the table lists the cementitious clinker phases formed in the samples and also indicates the presence/persistence of KCl.

Table 5: Cementitious phases produced in samples prepared for the title study. The presence of KCl is also shown. X denotes that the compound id not present while a circle (●) denotes that the compound is present. The sample ID indicates the temperature at which the samples were thermally treated except for the S-CBPD samples where all samples were heated to 1200 °C. The label "P" in the sample names indicates the pelletised samples. The detailed Al/Fe ratio was not determined for ferrite phases in the present work.

Sample ID	Heating time (min)	C_3S	C_2S	$C_{12}A_7$	$C_2(A_xF_{1-x})$	CA	CA_2	KCl
Raw CBPD	-	X	●	X	●	X	X	●
CBPD_900	120	X	●	●	●	X	X	●
CBPD_900_P								
CBPD_1100	30	X	●	●	●	X	X	●
CBPD_1100_P								
CBPD_1100	60							
CBPD_1100_P								
CBPD_1100	120							X
CBPD_1100_P								
CBPD_1200	30	●	●	●	●	X	X	X
CBPD_1200_P								
CBPD_1200	60							
CBPD_1200_P								
CBPD_1200	120							
CBPD_1200_P								
C_3S_1200	30	●	●	●	●	X	X	X
C_3S_1200	60							
C_3S_1200	120							
C_2S_1100	30	X	●	●	●	X	X	●
C_2S_1100	60							
C_2S_1100	120							X
$C_{12}A_7$_1100	30	X	●	●	X	●	●	●
$C_{12}A_7$_1100	60							X
$C_{12}A_7$_1100	120							
S-CBPD 1 (-)	30	X	●	X	X	X	X	X
S-CBPD 2 (KCl)								
S-CBPD 3 (Al_2O_3)		X	●	●	X	X	X	
S-CBPD 4 (Fe_2O_3)		X	●	X	●	X	X	
S-CBPD 5 (MgO)		X	●	X	X	X	X	
S-CBPD 6 ($Ca_2SO_4.2H_2O$)								

XRD patterns of the CBPD heated at 900°C, 1100°C, and 1200°C are shown in Figs. 4, 5, and 6 respectively. It should be noted that in the annotated XRD Figures, the ferrite assemblages: $C_2(A_xF_{1-x})$ where $0< x <1$, are undifferentiated. The CBPD heated at 900°C (Fig. 3), in both powder and pellet forms, showed similar patterns suggesting no significant advantage through pellet pressing. $Ca(OH)_2$ present in the original CBPD was not observed in the sample heated at 900°C, suggesting that $Ca(OH)_2$ has dehydroxylated. Mayenite, $C_{12}A_7$, a major phase in calcium aluminate cement clinker, is present, and silica has reacted to form belite C_2S (no SiO_2 is observed in Fig 4). However, KCl which is unwanted in the final clinker remains after two hours of heating even though the peak intensity appears to be lower compared with the original CBPD. Chloride is known to substitute into the mayenite structure; however, it is not clear whether any Cl has incorporated into the mayenite.

The CBPD heated to 1100°C (Fig. 5) showed the presence of belite and mayenite. The KCl content appears to decrease with heating time and is no longer observed after 120 minutes of heating. Similarly, as shown in Fig. 6, upon heating to 1200°C, the peaks of KCl are not discerned even after only 30 minutes of heating. This can be explained by the difference in the vapour pressure of KCl at the different temperatures; vapour pressure data is provided in Fig. 7. The vapour pressures of KCl at 1100°C and 1200°C are significantly higher than that at 900°C, and thus, KCl can evaporate easier at these higher temperatures.

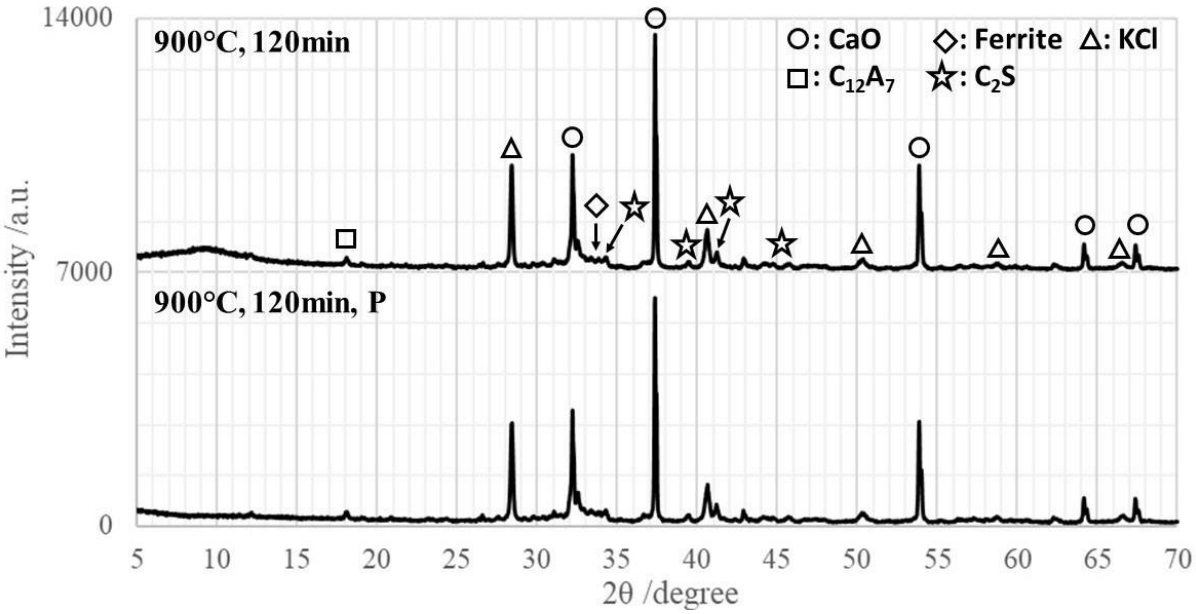


Figure 4: X-ray diffraction patterns of the cement kiln bypass dust heated at 900°C for 120 min showing the difference between pelletised and unpelletized samples. The label "P" denotes the pelletised sample.

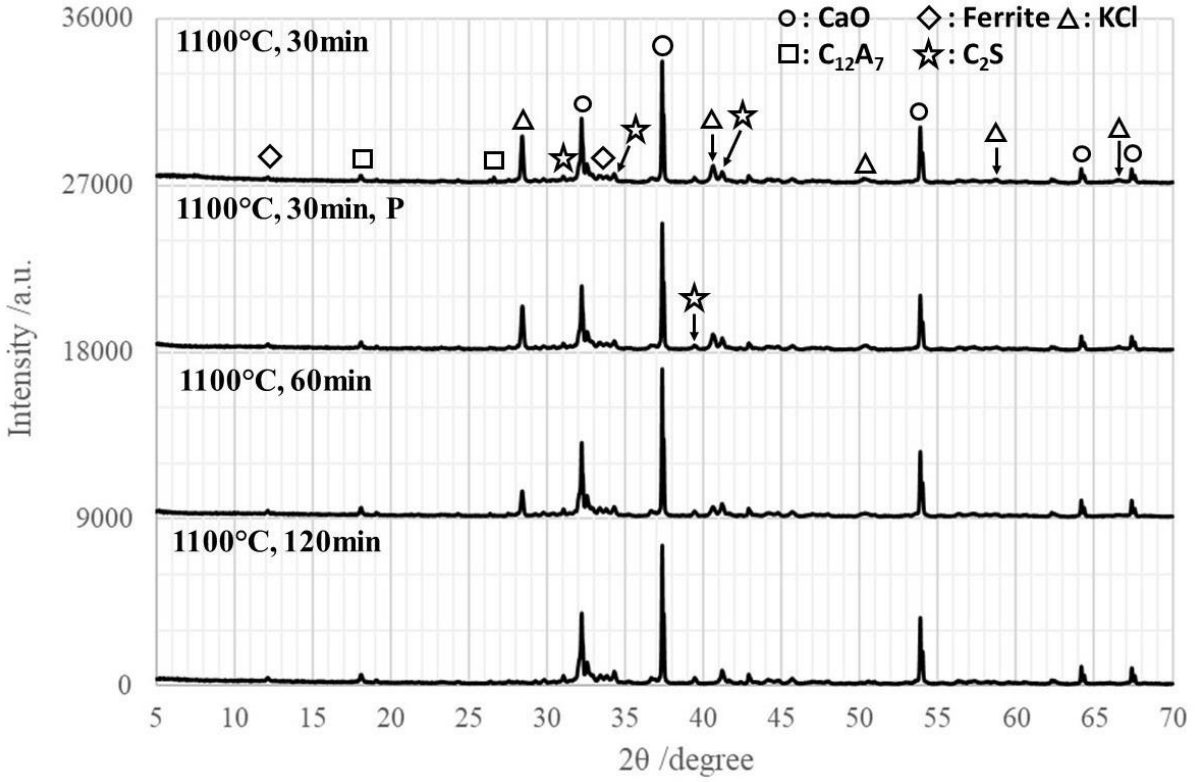


Figure 5: X-ray diffraction patterns of the cement kiln bypass dust heated at 1100°C for 30, 60, and 120 min. The label "P" denotes the pelletised sample.

Unexpectedly, all the samples heated to 1200°C showed the formation of alite which is normally produced industrially at temperatures greater than 1400°C and thermodynamically unstable below 1250°C [19]; pure alite is usually formed in-lab at higher temperatures of 1600°C [20]. This is a significantly lower temperature than normally used in the cement industry for alite formation. Components in the CBPD contributed to lowering the formation temperature of alite and enhancing its formation; however, the exact mechanism is still not apparent.

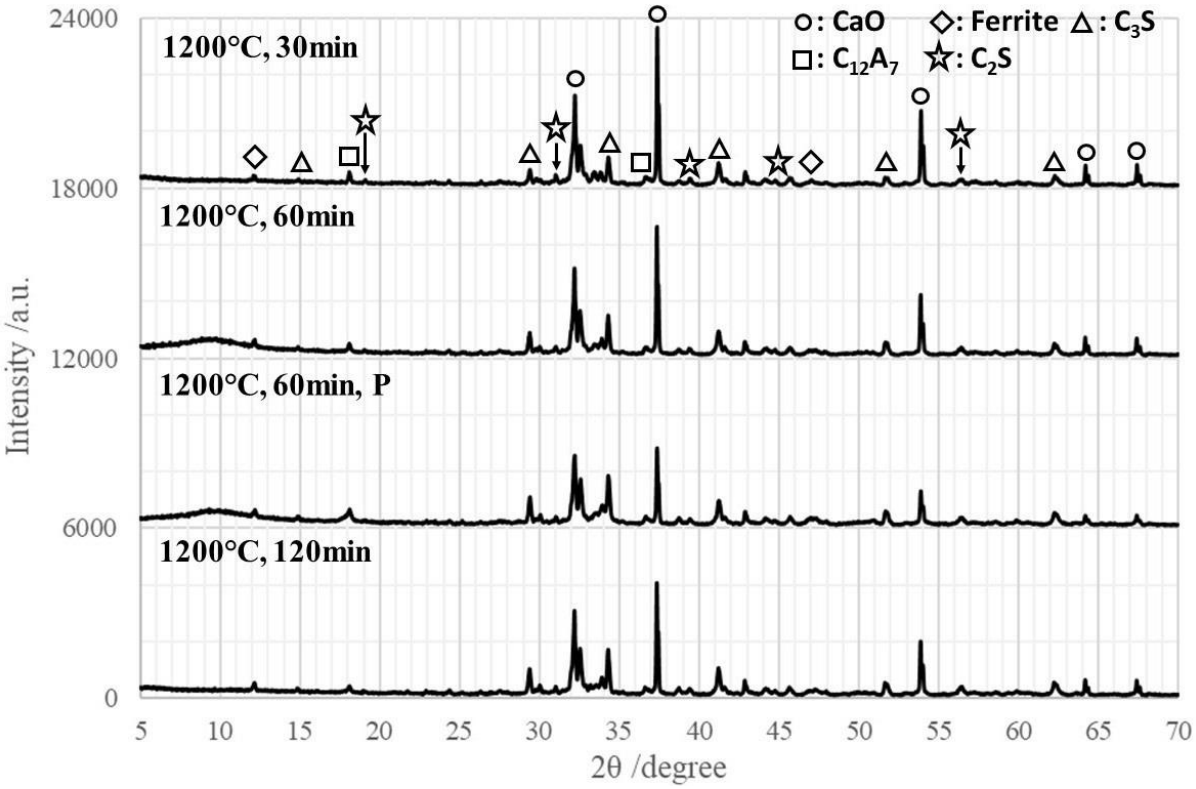


Figure 6: X-ray diffraction patterns of the CBPD samples heated at 1200 °C for 30, 60, and 120 min. The sample labelled "P" denotes the pelletised sample.

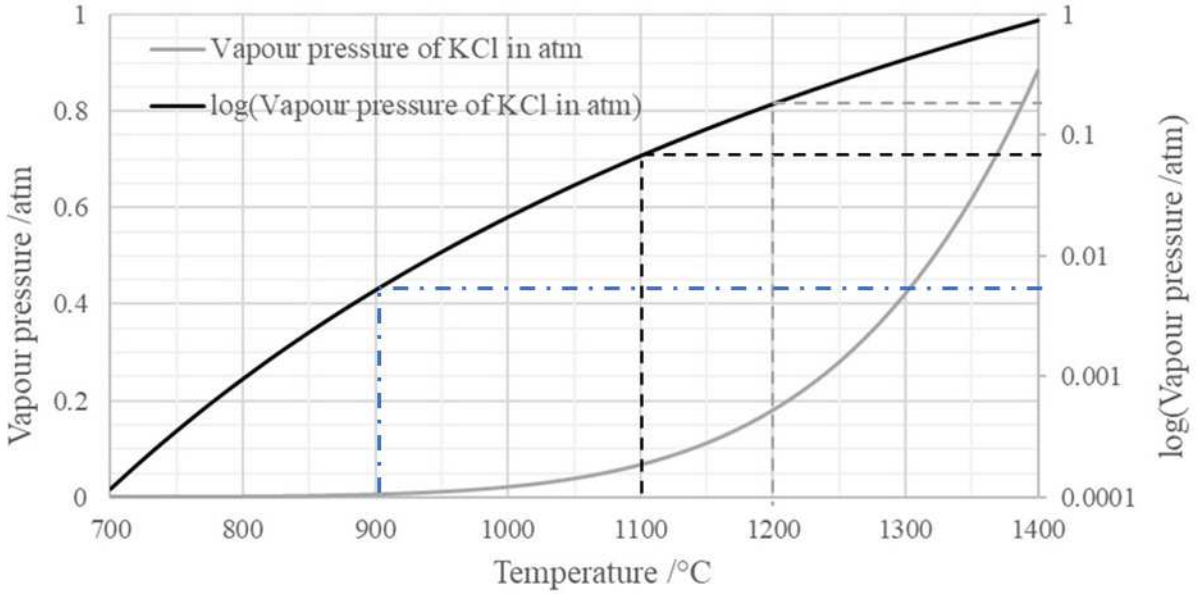


Figure 7: The vapour pressure of potassium chloride as a function of temperature. The left;primary axis shows a linear scale (grey line) while the right;secondary axis shows a logarithmic scale of the same data (black line). The data is taken from the Dortmund Data Bank for saturated vapor pressure calculations (available at: http://www.ddbst.com/en/EED/PCP/VAP_C4577.php).

It was noted that the weight of samples decreased by approximately 20% on average after heating at 1200°C, which agrees well with the thermogravimetric analyses shown in Fig. 3. There was no significant difference between samples in powder and pellet forms in the range of heating temperatures and heating durations tested; hence, only powder samples were produced in further experiments.

4.3. Interaction of CBPD with additives: results

Figure 8 shows the XRD patterns of the CBPD samples with additional silica targeted to produce alite at 1200°C. As shown in the figure, when additional silica was introduced, the peaks for alite and belite clearly became more intense compared with the previous CBPD samples heated at 1200°C without any additions (Fig. 6). However, it is apparent that significant quantities of free CaO are present and did not completely react with belite to form

alite. This may suggest the limited reaction between CaO and belite in the conditions tested. As observed in the CaO-SiO_2 phase diagram presented in Fig. 9, C_3S formed at high temperatures can decompose into CaO and C_2S at lower temperatures; however, due to the low quantities of material processed and the temperature of the ambient (~20°C), the produced clinker can be assumed to have been quenched; thus, decomposition of alite during the cooling of the samples would not have occurred. Either way, the tested conditions designed to utilise all Ca component of CBPD for the formation of alite was insufficient for the complete conversion to alite at 1200°C, but sufficient to manufacture a clinker that contains alite as a major phase.

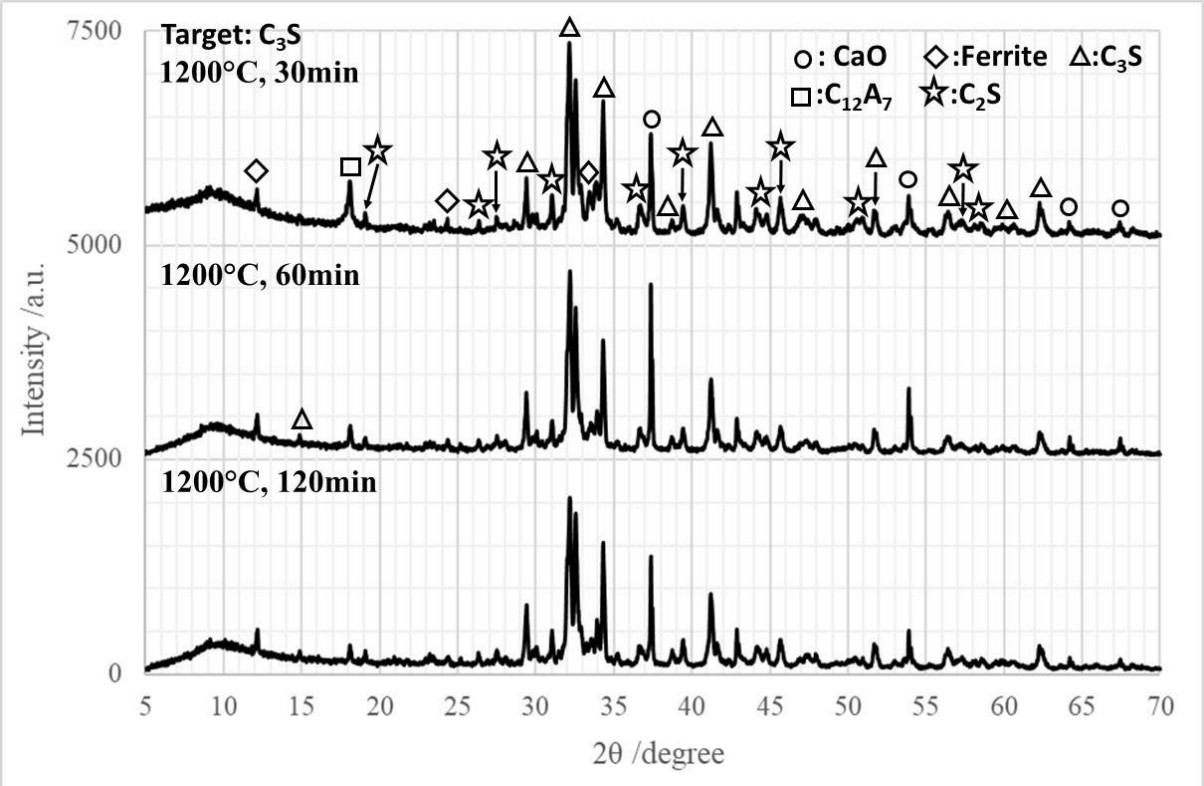
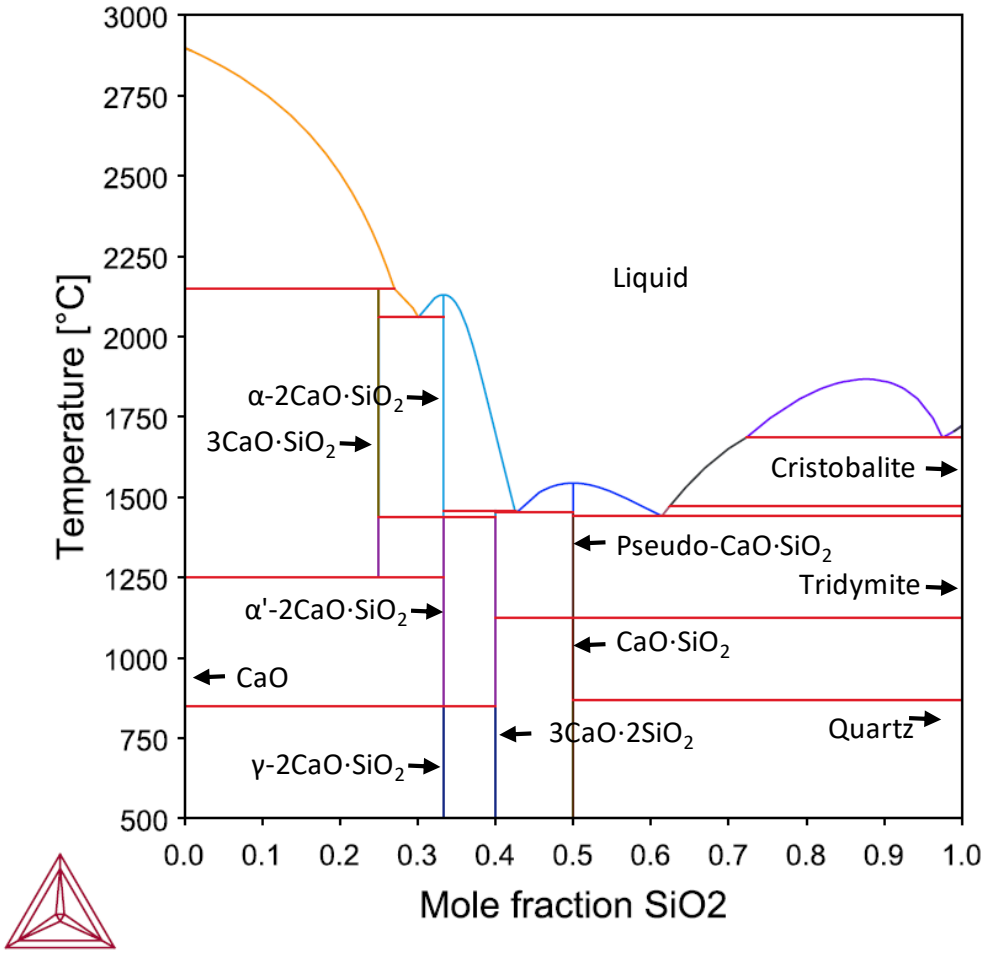


Figure 8: XRD patterns of the cement kiln bypass dust samples mixed with silica for creating alite at 1200 °C while heating for 30, 60, and 120 minutes.



295

296 *Figure 9: CaO-SiO_2 phase diagram was calculated using Thermo-Calc Software [21] with Thermo-Calc Software OXDEMO:*
297 *Oxide demo database v2.0*

298 XRD patterns of the CBPD samples with additional silica targeted to produce belite (C_2S) at
299 1100°C are provided in Fig. 10. A significant increase in intensity is observed for the peaks of
300 belite when compared with the CBPD samples heated without any additions. The XRD
301 patterns also showed the presence of SiO_2 (cristobalite) at ~22° 2θ which is a high
302 temperature polymorph of unreacted SiO_2, which decreases when reaction time is extended
303 to 120 minutes. The presence of any unreacted SiO_2 may be attributed to some of the CaO in
304 CBPD being combined as mayenite and ferrite, which were nit targetted.

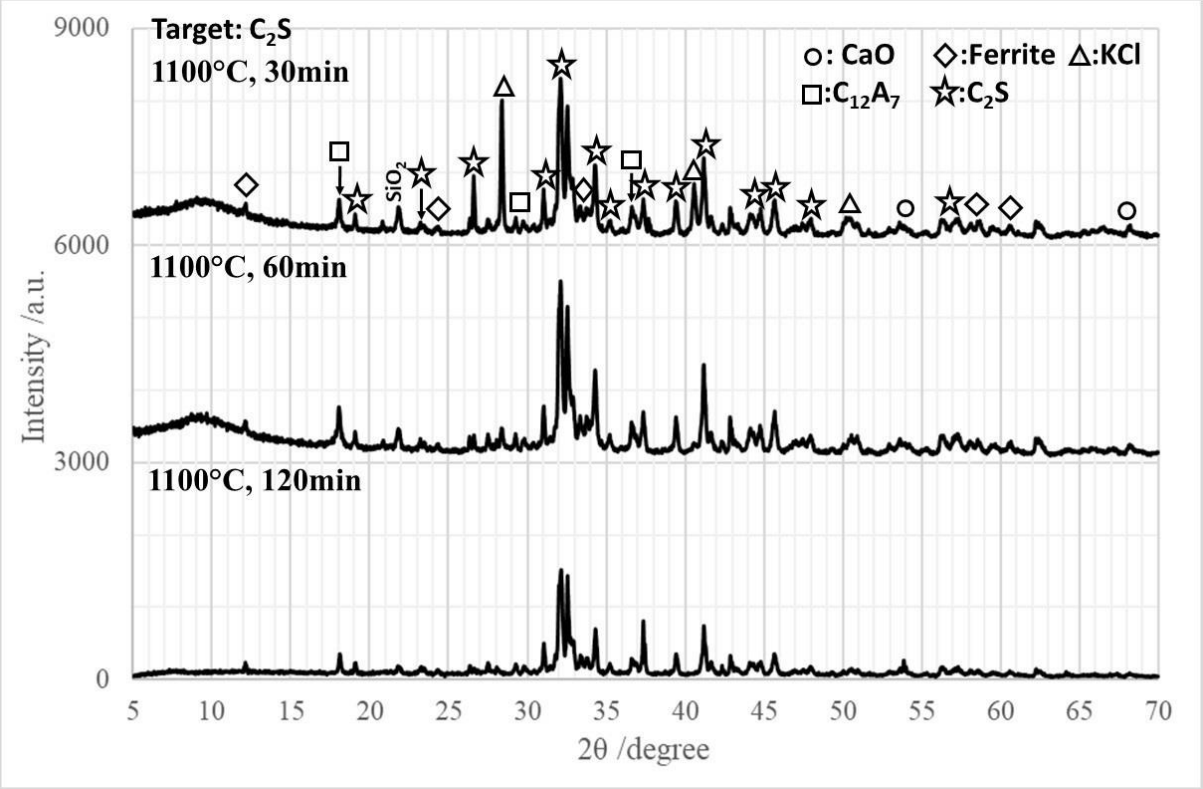


Figure 10: XRD patterns of samples mixed with silica for creating belite at 1100 °C while heating for 30, 60, and 120min.

The XRD patterns of the samples with additional alumina targeted to produce mayenite ($C_{12}A_7$) at 1100°C are also provided in Fig. 11. A clear increase in mayenite content was observed when compared with the CBPD samples heated at 1100°C without any additions. This system also produced a significant amount of mono-calcium aluminate (CA) and trace amount of CA_2. CA is a known cementitious phase whereas CA_2 is weakly hydraulic [22]. The production of CA and CA_2 can be attributed to some of the CaO in CBPD being combined as belite and ferrite. The reactions of CBPD at 1100°C targeting belite or mayenite suggest that the production of belite and mayenite from CBPD can be increased by adding silica or alumina and that there was minimal unreacted SiO_2 or Al_2O_3 after 120 minutes. They also had minimal to no free lime (CaO). The interaction of CBPD with additional silica or alumina resulted in the

formation of both targeted and untargeted hydraulic phases; this shows that the CBPD is favourable for the formation of various cementitious clinker phases and phase assemblages.

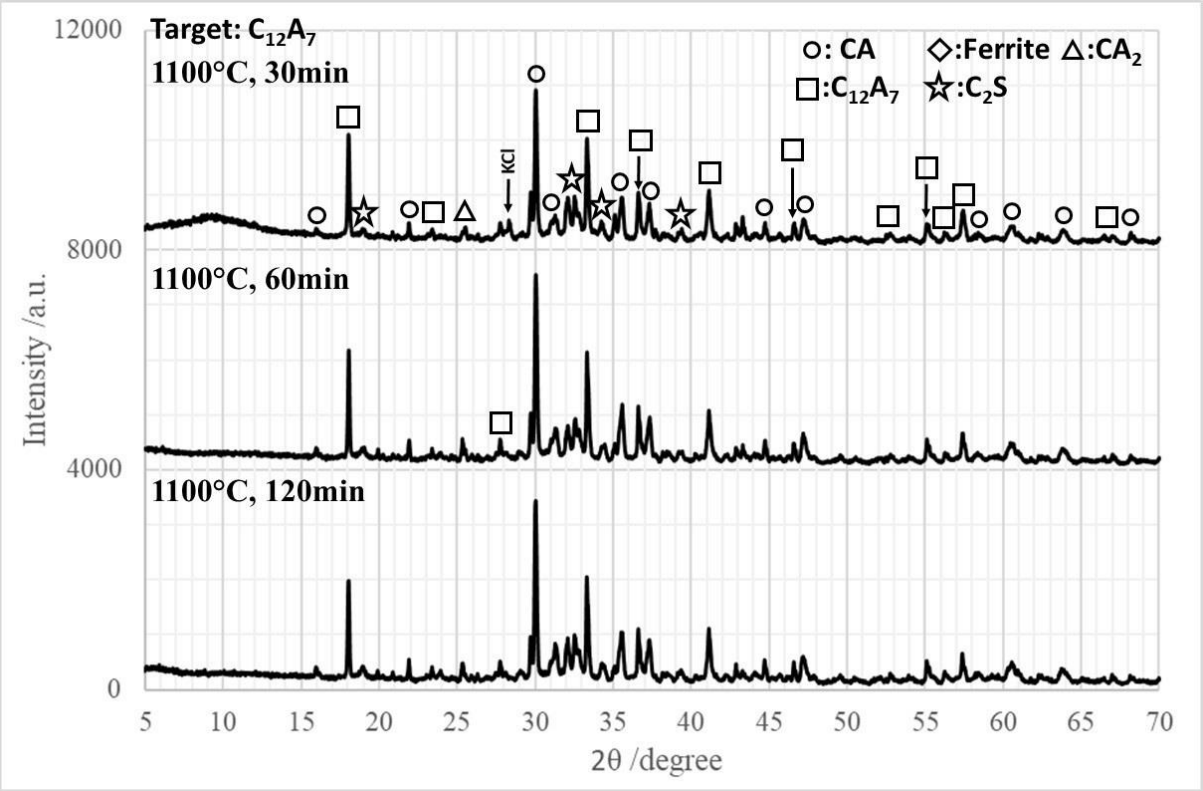


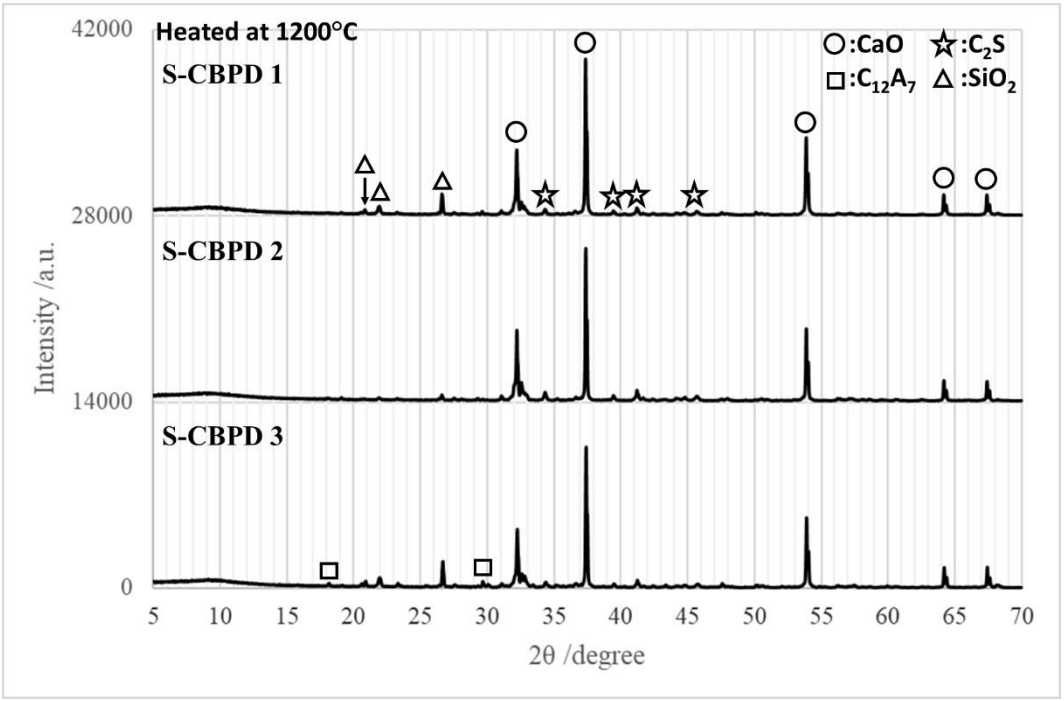
Figure 11: XRD patterns of samples mixed with alumina for creating mayenite at 1100 °C while heating for 30, 60, and 120 minutes.

It should be noted that there was a gradual decrease in the intensity of KCl peaks in the samples heated at 1100°C, while no peaks of KCl were observed when heated at of 1200°C even as short as 30 min; consistent with that found in CBPD samples without additives. This loss of KCl at early stage (within 30 min) could be potentially one of the reasons for the limited combination of CaO at 1200°C. As previously mentioned, such salts can act as a flux to improve the extent of reactions [14]. Further study is necessary to elucidate this point.

4.4. Behaviour of simplified CBPD: results

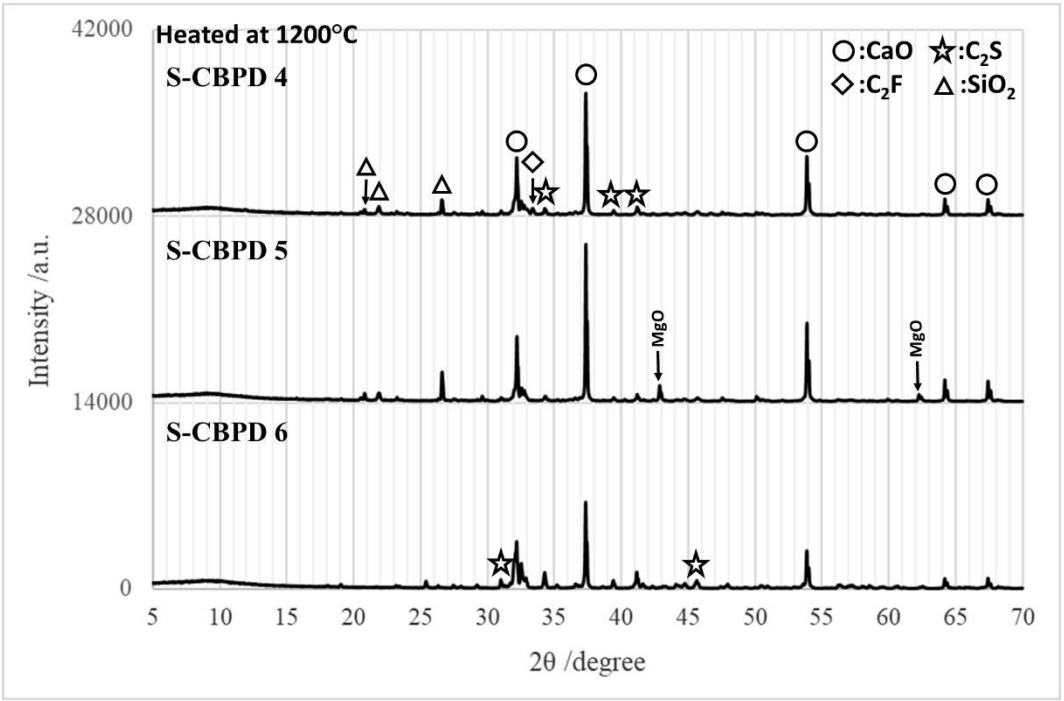
One of the key findings in the previous sections was the formation of alite from CBPD at 1200°C both with and without additional silica added. The effects of major constituents in CBPD on the reactivity of the system were studied by making “simplified CBPD” composed of $CaCO_3$ and SiO_2 alone and with one other constituent shown in the elemental analyses of raw CBPD namely: KCl, Al_2O_3, Fe_2O_3, MgO, and $CaSO_4.2H_2O$.

The diffraction patterns for the “simplified CBPD” samples are shown in Figs. 12 and 13. The significant reduction of the peak intensity of SiO_2 in S-CBPD 2 confirms that KCl does indeed enhance the formation of belite. The sample with added gypsum also showed lower intensity peaks for silica, suggesting the enhanced reaction of silica. The peak intensity for CaO also appears to be lower in the system with added gypsum. However, no other calcium silicate reaction products were identified. In addition to belite, the formation of mayenite was observed through adding Al_2O_3 while dicalcium ferrite (C_2F) was formed with the addition of Fe_2O_3. The presence of MgO appears to have a limited participation in the reaction of the system.



344

345 *Figure 12: X-ray diffraction patterns of the "simplified" CBPD samples prepared from $CaCO_3$, SiO_2, and a third additive: 1 =*
346 *no additive; 2 = KCl; 3 = Al_2O_3.*



347
348 *Figure 13: X-ray diffraction patterns of the "simplified" CBPD samples prepared from $CaCO_3$, SiO_2, and a third additive: 4 =*
349 *Fe_2O_3; 5 = MgO; 6 = $CaSO_4.2H_2O$.*

350

None of the S-CBPD samples produced alite; therefore, it can be inferred that the formation of alite by pyro processing CBPD at 1200°C with and without addition of silica is due to a synergetic effect between the constituents, for example, that the presence of S and Cl may have allowed for the formation of chlorellestadite ($Ca_{10}(SiO_4)_3(SO_4)_3Cl_2$) which may enhance alite formation [23]; however, no chlorellestadite was detected through XRD. The presence of iron in the clinker raw-mixes has also been found to aid alite formation at lower temperatures in the presence of a flux [24], and this may have also been a contributing component.

5. Further discussion

The present work shows that CBPD can be thermally treated to produce clinker phases at lower temperatures than is conventional. Real life applications can involve pyro processing CBPD with other raw materials such as aluminosilicate clays to produce modified cement clinker or even supplementary cementitious material free from uncombined CaO. However, this may not be directly applicable in existing kiln configurations due to the volatilisation of salts which were an initial reason for the bypass dust being withdrawn/generated. Nonetheless, another calcination process, not utilizing the traditional counter-current kiln can be employed for the pyro processing of raw material feed containing significant amounts of CBPD. For example, the new process can be a batch reactor with a salt separation/deposition system. The collected salt can then be used as commodity or in another process or recycled for the manufacture of cementitious materials using other calcareous and aluminosilicate raw materials. Additionally, due to the lower temperatures required for clinker phase

manufacture in the presence of the salt/KCl, it may be possible to use indirect or electrically heated furnaces; which, if powered from sustainable/green sources, will result in the production of a zero-carbon cementitious material as their will be minimal associated chemical and process carbon emissions. Lower formation temperatures can also enable the utilisation of lower quality alternative fuels such as biomass; nonetheless, further work is required to optimise clinker or SCM production and formulations from CBPD and design of a new calcination process/unit.

The composition of CBPD will vary by location of the plants due to changes minor constituents of fuels and local raw materials, as well as plant configurations where CBPD may be combined with CKD; however, these variations can be managed through blending with additives during raw-mix design of material to be processed. While the industrial pyro processing of CBPD will most probably require capital investment in any cement plant, this could be cost competitive since the costs of transport and landfill are generally high.

The valorisation of CBPD for clinker manufacture will also contribute to reduce the cost of CO_2 emission, as the CBPD is a source of already decarbonised CaO, which is key for clinker manufacture. The reduced formation temperature of clinker phases can also translate to a reduction energy demand and in fuel-derived CO_2 emissions when compared to the conventional Portland cement manufacturing process. Additionally, unlike limestone rock, the CBPD will not require grinding prior to pyro processing.

The properties of hardened cement made from clinker produced through the pyro processing of CBPD still needs to be assessed in terms of its chemical, rheological, mechanical, and

durability performance. The work here has shown that the Cl-containing salt(s) can be driven off through the heating process, but the effects of any Cl remaining in the cement is still unknown. Additionally, the effects of any potential substitution or persistence of alkali (e.g., potassium) in the clinker/cement and subsequent concrete material will need to be assessed.

In agreement with previous works [15, 16], the formation of belite and mayenite is observed in this work at temperatures as low as 900°C in the presence of a molten-salt flux. However, the final product still contained the salt after cooling from 900°C. Future works should also attempt to produce cement phases at such low temperatures while optimising the amount of salt in the mix before and after thermal treatment; other molten salts can also be tested. Previous studies [25, 26] have also shown that the CBPD which contain large quantities of undesired constituents, such as chlorides, may be classified or separated mechanically to reduce the quantities of these undesired constituents to required limits.

6. Conclusions

Cement kiln bypass dust can be valorised through thermal treatment for the manufacture of cement clinker or supplementary cementitious materials. The formation of cement clinker phases such as belite, mayenite, alite, and ferrite is enhanced by the minor components intrinsic to CBPD, in particular KCl. Clinker Phase formation temperatures can be reduced, and reaction kinetics can be improved when compared to the utilisation of the conventional raw materials. Silica and alumina containing raw materials can be mixed with the CBPD, before firing, to produce complete cement clinker phase assemblages and free of uncombined CaO.

413 The formation of alite at 1200°C is a significant observation of this work. It suggests that CBPD
414 can potentially be used to produce alite based cements (e.g. Portland cement) at lower
415 temperatures than that of the conventional process. The exact mechanism for the low
416 temperature alite formation observed through the thermal treatment of CBPD requires
417 further investigation but it is apparent that the intrinsic chloride salt plays a vital role.

418 By heating at temperatures as low as 1100°C, the salt is removed/evaporated from the system
419 leaving behind a cementitious product free from majority of the undesired alkali chlorides
420 and other undesired salts which are initially present. The produced clinker phases have a
421 lower production temperature and thus can have lower fuel-derived CO_2 emissions.
422 Additionally, the CaO in CBPD exists in an already decarbonised form; therefore, the clinker
423 produced from CBPD has a lower raw-material CO_2 footprint than conventional cement
424 clinker produced from the virgin raw materials. Outcomes of this work also encourage
425 attention to the use of chloride salts as a flux for cement clinker manufacturing.

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