ACCELERATED CARBONATION FOR THE TREATMENT OF LANDFILLED CEMENT KILN DUST

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Accelerated Carbonation Technology (ACT) can be used to treat a wide range of alkaline wastes and metal-contaminated soils by exposing them to a carbon dioxide rich atmosphere in a way that promotes the massive precipitation of calcium carbonate. The material obtained has improved physical and chemical characteristics. This work presents the characterisation of historically deposited cement kiln dust (CKD) and its potential reactivity with carbon dioxide gas. The CKD investigated originated from a landfill, up to one hundred years old. The bulk chemical composition was determined by X-ray Fluorescence (XRF), the mineralogy of the untreated and carbonated CKD by X-ray Diffractometry (XRD) and the change in microstructure upon carbonation was examined by Scanning Electron Microscopy (SEM/EDS). Key characteristics of treated and untreated CKD such as carbon dioxide uptake, pH, and moisture content are presented and discussed.

INTRODUCTION

Accelerated Carbonation Technology has been successfully used to treat a broad range of industrial wastes and contaminated soils (Fernandez-Bertos *et al.,* 2004; Johnson, 2000).

In the UK, 11.7 million tonnes of cement are manufactured each year (BCA, 2007). This process generates very fine dusts called cement kiln and cement bypass dust, collected from the exhaust gases by air pollution control devices (Sreekrishnavilasam *et al.,* 2006). It is estimated that 110,000 tonnes of cement dusts are generated annually in the UK (BCA, 2007). Efficient modern cement plants now return a large proportion of the CKDs into the manufacturing process, but in the past these were disposed to landill, and large amounts of landfilled CKD can be found in the south east of England. CKDs are highly alkaline (12.5 - 13) and are classified as hazardous waste. In unlined landfills, the dusts pose a risk by the leaching of alkalies upon contact with rain or groundwater and consequently the release of metal contaminants.

Cement manufacture process also generates large amounts of carbon dioxide gas from the burning of kiln fuel and the calcination of the limestone. The CO_2 emitted amounts to 2% of the UK's total carbon dioxide generation.

This paper investigates the properties of landfilled cement dusts, their microstructure and ability to bind carbon dioxide, with a view to their potential reuse.

MATERIALS AND METHODS

Raw Materials

Four cement kiln dust samples were extracted by dry coring from a former industrial landfill in the south-east of England (see table 1). Dumping of CKD at the un-lined site took place for nearly a century, and 1 million tonnes of CKD were disposed of this way. The CKD is unconsolidated, highly alkaline and contains heavy metals. The as received CKDs were examined for moisture content and pH (BS1377-3).

Table 1. Sample name and depth of CKD

Sample	Depth
CKD 2	Surface (active site)
CKD 3	1 m (active site)
CKD 15	Surface (disused site)
CKD 7	3 m (disused site)

Treatment method

CKDs were mixed with water in a rotary pan mixer under a flow of carbon dioxide gas. The partially carbonated dusts were stored in a 100% carbon dioxide atmosphere for 24 hours, by which time they were fully carbonated. A loss on ignition method (Heiri *et al.,* 2001) was used to measure carbonate content.

X-ray Fluorescence

Major elements in the dusts were measured as fused beads (64% lithium tetraborate, 34% lithium metaborate flux, XRF Scientific Ltd) and analysed with a Philips LW1400 spectrometer. NIST cement standards (633, 635, 638, 1881, 1882, 1883) were used for instrument calibration.

X-ray Diffraction

A Siemens D500 diffractometer was used to perform the analyses upon both the dried as-received (uncarbonated) and carbonated dusts. The source of radiation used was CuKα at an accelerating

voltage of 40 kV and 30 mA. Pressed powder mounts were prepared from dried and crushed CKD and scanned from 5° to 65° 2-theta in 0.02° steps. Interpretation of the X-ray spectra was carried out using DIFFRAC^{plus} EVA software by Bruker AXS.

Scanning Electron Microscopy
Scanning electron microscopic analysis of resin (Buehler Epo-thin) blocks prepared from the treated and untreated CKDs were carried out using a JEOL JSM-5310LV microscope equipped with an Energy Dispersive Spectrometer (EDAX).

RESULTS

Characterisation of untreated CKD

Physical properties
The moisture contents of the landfilled CKDs varied between 12-15% for the samples located at the surface of the site and between 16-24% for those at depth.

Bulk chemistry
Landfilled cement kiln dusts had variable bulk composition. The main elements (as oxides) were Ca, Si, Al, S, Fe, Mg, Na and K, as shown in Table 2.

Table 2. Oxide compositions of the raw materials

Oxide	CKD2	CKD3	CKD7	CKD15
CaO	41.1	27.3	34.2	41.8
Al_2O_3	4.3	7.6	6.7	3.9
SiO_2	18.5	32.2	31.0	15.0
Fe_2O_3	2.0	2.8	2.7	2.0
Na_2O	0.4	1.1	1.2	0.1
K_2O	1.6	1.9	2.5	0.5
MgO	3.5	4.5	1.2	0.9
SO_3	4.7	2.5	3.3	3.5
Minors	0.5	0.8	0.7	0.5
LOI (950°C)*	22.5	18.6	15.1	30.1

*LOI – loss on ignition
Values in weight %

The CKDs had variable calcium content, ranging from 27.3% to 41.8%. This is in good agreement with literature reporting the composition of landfilled CKD (Siddique, 2006; A. Sreekrishnavilasam et al., 2007)
The LOI varied greatly in the CKDs analysed, and is related to depth in the landfill. CKDs are susceptible to natural carbonation, which occurs more rapidly in materials directly exposed to the atmosphere. Therefore, it was expected that the CKDs nearer the surface of the landfill were more highly carbonated and exhibited a higher LOI.

Characterisation of treated CKD

Physical Properties
Mixing the CKDs in the pan mixer had the effect of eliminating the fine fraction from the materials through aggregation. In most cases the mixing action affectively granulated the dusts into irregular lumps and rounded pellets (see Figure 1). This improved the mechanical properties of the dusts, and reduced surface area. The physical properties of ACT-treated CKD will be discussed elsewhere.
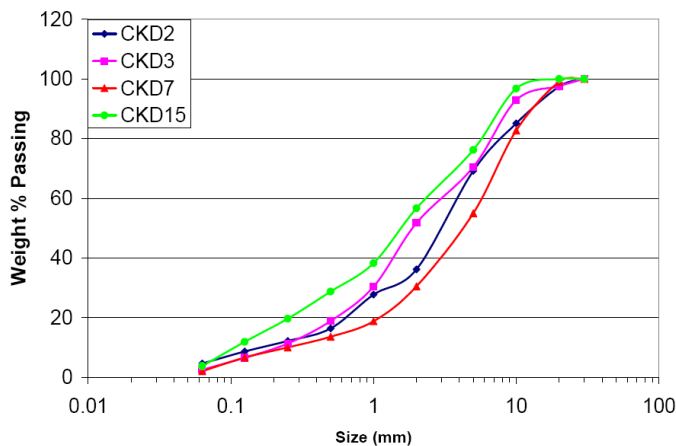

Figure 1: Particle size distribution of untreated CKDs (according to BS EN 933-1)
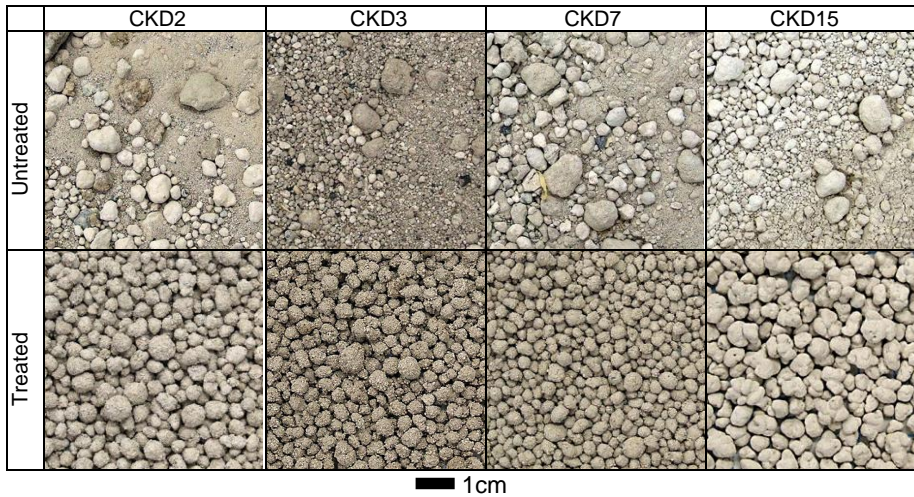
Figure 1. Photographs of untreated and treated CKDs

pH and carbon dioxide uptake

Unconsolidated landfills containing highly corrosive waste pose a risk for the environment through leaching of alkalis and toxic metals. By treating CKD with carbon dioxide pH was significantly reduced. The natural pH and that obtained after ACT are shown in Figure 3.
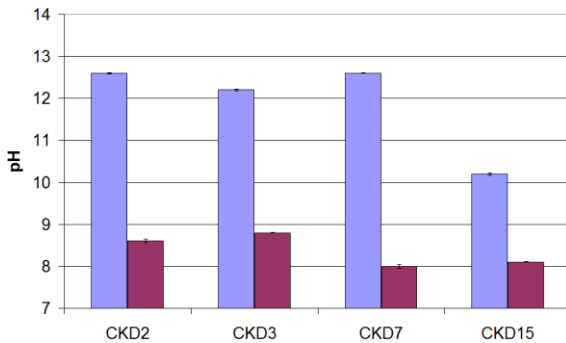

Figure 3. pH of the CKD before and after ACT

The pH of the untreated CKD was between 12.2-12.5, except for CKD15, which had a pH close to 10. The low pH of this sample was due to its high degree of carbonation which occurred in the landfill environment, however the exposure timescales involved are unknown. Nevertheless, treatment by ACT over 24 hours decreased the pH of the CKD's to below 9.0 and in respect of CKD7, to a pH or 8.0.

During ACT, the amount of carbon dioxide uptaken by the CKDs was up to 8.5% by weight and a very good correlation was observed between the calcium content and the uptake of carbon dioxide by the CKD's. It can be clearly seen that the increase of calcium content resulted in increased carbon dioxide uptake. However, CKD15 was the exception, in that despite having a high Ca content the carbon dioxide uptake was relatively low at 2.3% by weight, and is attributed to the effects of weathering in landfill and a high degree of natural carbonation by exposure to atmospheric CO_2.
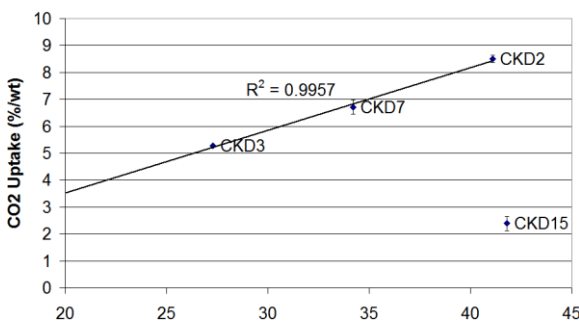

Figure 4. Carbon dioxide uptake and calcium content of the landfilled CKDs

X-ray Diffraction

XRF analysis revealed that the CKDs contain high percentages of calcium and magnesium, suggesting a high degree of reactivity with carbon dioxide. However, the reactivity of CKD depends on the nature of the phases present. The main crystalline phases identified by XRD in the untreated CKDs are shown in Figure 5. The highest intensity peak corresponds to calcite formed during the

exposure to the atmosphere in the landfill. All CKDs contained calcite, however, CKD15 was almost entirely carbonated, which and this would explain the high LOI and low pH recorded for this dust. Despite the high degree of carbonation of CKD15, low intensity peaks of ettringite were identified. Ettringite is commonly observed in landfilled CKD and is formed as a result of water percolation through the landfill. Ettringite is stable at higher pH's. The sample containing the most abundant ettringite was CKD7. Other phases identified in the landfilled CKD include quartz, portlandite, feldspar, hemihydrate and small amounts of non-reacted cement phases (C_2S, C_3S).
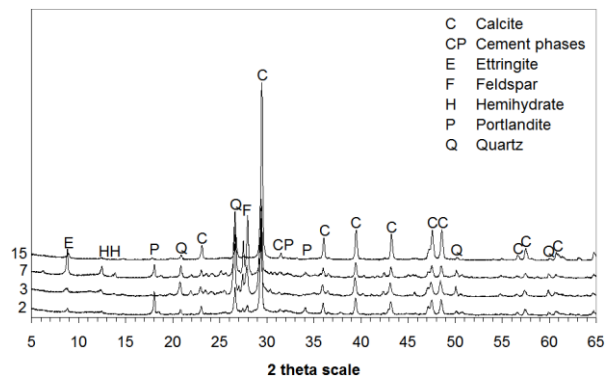

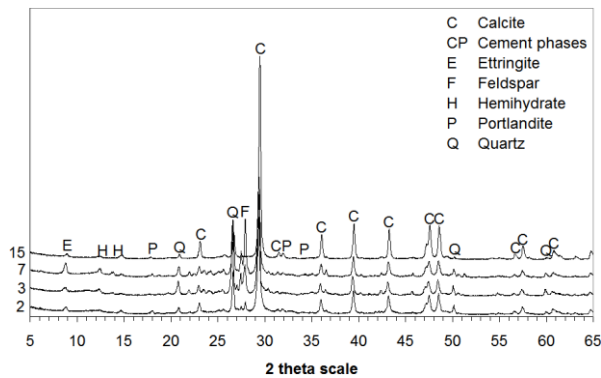Figure 5. X-ray diffractogram from CKDs, before the treatment by ACT

Figure 6. X-ray diffractogram from CKDs, after the treatment by ACT

Calcium oxide ('free lime') was previously reported as being present in CKDs (Siddique, 2006; Peethamparan et al., 2008) in significant amounts ranging from as little as 1% to 20-30%. The four landfilled CKDs examined here did not show any characteristics peaks for free lime. In general, on disposal to landfill the free lime is hydrated to portlandite, (Figure 6) and this is consistent with the reported behaviour of CKD in storage (Siddique, 2006).

Following ACT (see figure 6), an increase in the amount of calcite was observed for all CKDs treated. The intensity of peaks corresponding to portlandite and ettringite were reduced significantly, especially in CKD 7 and CKD2.

Scanning electron microscopy

From the four CKDs discussed, three were analysed for changes in microstructure upon ACT (see Figures 7, 8, 9). These exhibited similar microstructures, comprising a fine grained (< 1µm) groundmass, intermixed with angular and subangular particles of quartz and feldspar, up to 100 µm across (see Figure 9, uncarbonated).

Calcium carbonate was identified in all the untreated CKDs, as localised masses of fine crystals of approximately 100-200 µm across (Figure 7) and clusters of well formed crystals and isolated grains dispersed in the matrix (Figure 8).
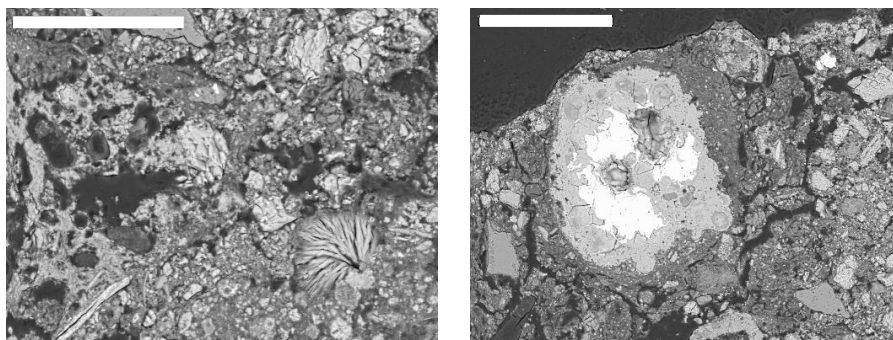

Figure 7. SEM backscattered electron image of uncarbonated CKD showing carbonate precipitate and ettringite (a) (scale 100 µm); hydrating clinker (b) (scale 200 µm)
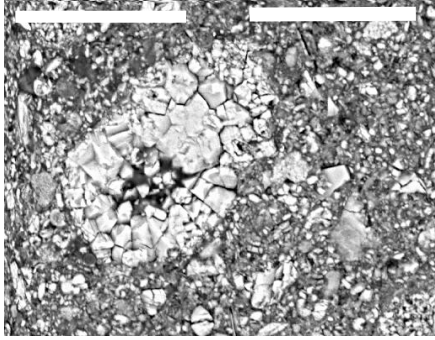
Figure 8. SEM backscattered electron image of well-formed calcium carbonate crystals (scale 50 µm)

Ettringite was observed in CKD3 and CKD7 as spherical clusters (Figure 7a) or as localised dense masses of euhedral crystals. Poorly crystalline aggregations of ettringite were also seen (Figure 8b).

The untreated CKD-matrix commonly contained clinker fragments, showing signs of hydration (Figure 7b), and large fragments (up to 150 µm in size) of iron oxide, barium sulfate, and traces of zinc and tin. The main consequence of the ACT treatment on the microstructure of carbonated CKD was matrix densifcation by precipitation of calcium carbonate (Figure 9).

Despite the low pH of the carbonated CKDs (below 9.5), clusters of ettringite were noted in the matrices, even at low magnifications (x75). The stability of ettringite to carbonation is thought to be related to the moisture content and pH. In dry conditions ettringite is decomposed within 3 days of exposure to CO_2, whilst at w/s ratios of approximately 3.0, it can persists for over a week (Klemm, 1998). The minimum pH beyond which ettringite ceases to be stable varies amongst authors. However, the lowest value reported was 9 (Stark and Bollmann, n.d) and work is required to explain the behaviour of this phase.
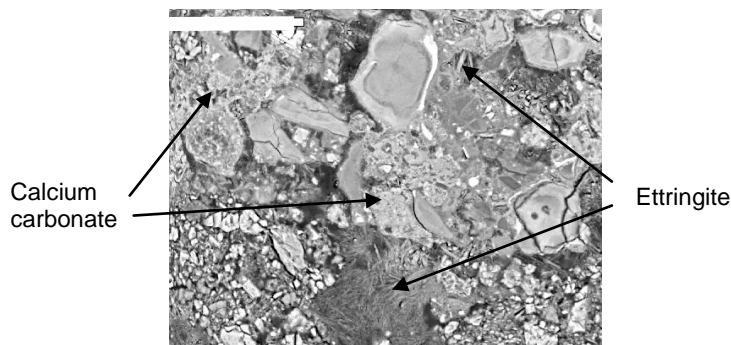

Figure 9. SEM backscattered electron image of a mixed area containing ettringite bordering carbonated matrix (scale 50 µm)
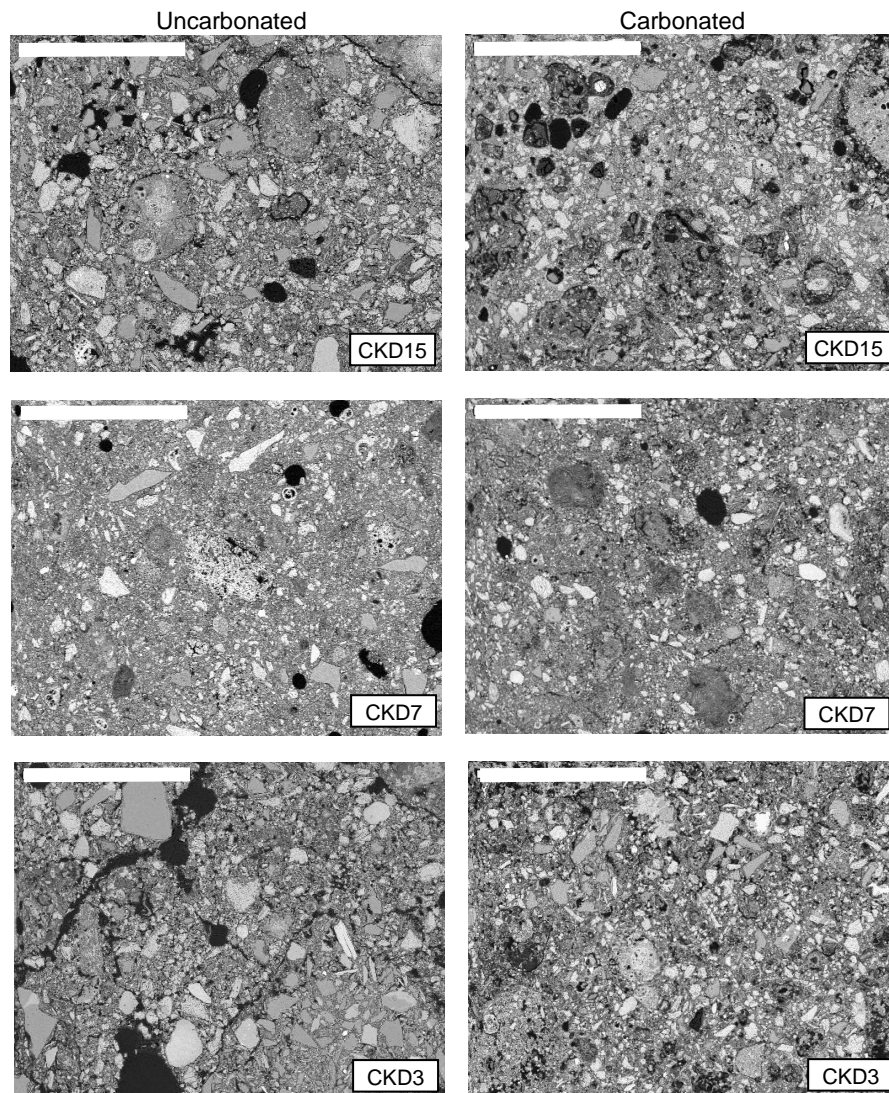
Figure 7. SEM backscattered electron images of uncarbonated and carbonated CKD (scale 500 μm)

CONCLUSIONS

Accelerated Carbonation Technology has been successfully applied in the laboratory to decrease the hazardous nature of landfilled cement kiln dusts. The results of the treatment by carbonation were:

a) pH was reduced from 12.2-12.5 to less than 9 after 24 h of exposure to carbon dioxide gas;

b) Samples reacted with between 2.3 to 9.5 % w/w of carbon dioxide which was permanently incorporated in the treated material as calcium carbonate;

c) the physical characteristics of the CKD were improved, through granulation and densification.

ACKNOWLEDGEMENTS

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