Incorporating Paint Sludge In The Manufacture Of OPC Clinker. Part I: The Effect On Burnability

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ABSTRACT

This paper describes the production of cement clinker containing some paint waste ash. The various raw mixes investigated, their characteristic parameters and the selection of the most successfully one for further work are given and some results from thermal investigations summarised. The burnability, grindability and microstructural composition during clinkering some of the material are also given.

INTRODUCTION

Wastes containing burnable organic materials are very common. Their disposal can cause considerable difficulties, because many of them are hazardous. Several sorts of waste can be successfully destructed in cement making rotary kilns, e.g. car tyres, sewage sludge, waste solvents from the pharmaceutical, paint and metallurgical industries, etc.[1]. From an environmental point of view, the destruction of hazardous organic wastes can be considered completely safe and numerous investigations have been carried out in this regard [2-7]. However, from a cement manufacturing point of view, their use as substitute fuels and/or raw materials could cause considerable difficulties, e.g. formation of adherent layers in the kiln because of volatile constituents and even changes in cement performance because of the incorporation of heavy metal elements in the clinker [8]. Despite the concerns mentioned, the use of waste derived fuels is nowadays a standard practice in many cement-making rotary kilns, and in some cases, even an additional source of income for the cement industry.

The effect of the incorporation of heavy metal elements into clinker as a result of waste burning and its consequent influence on the performance of cement have been previously described in the literature [8-15]. However, in most of the reports to date, the heavy metal elements have been added individually to the raw meal as a salt before the subsequent clinker was manufactured and investigated. However, there were only limited reports in literature where a waste containing one or more heavy metal elements have been added to the clinker raw materials and the Portland cement produced from it investigated [16]. Furthermore, most of the previous investigations focused their attention on the incorporation of the heavy metal elements into the clinker microstructural phases and the subsequent effects on setting times and strength development behaviour, with little attention to the effect on burnability.

It was therefore decided to investigate the use of paint sludge waste as a possible fuel substitute and the consequent effect of the resultant ash on the

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burnability of Portland cement clinker. For this purpose raw meals were constituted from the normal constituents typically used for the manufacturing of clinker, as well as small quantities of the paint waste ash, which would be incorporated into the raw meal during the production process, should it be used as a partial fuel substitute. Various aspects of the production of the resulting clinkers were investigated, e.g. their burnability, grindability, and microstructural composition. This paper will describe the findings of and observations made during this investigation. Suggestions for further experimental work to be described in subsequent papers will also be made.

EXPERIMENTAL PROCEDURE

Pressed pellets and fused beads were prepared of each material according to standard methods [17,18] and analysed on a Siemens MRS 400 X-ray fluorescence (XRF) spectrometer. The chemical compositions, as determined by XRF analysis, of the materials used in this investigation are summarised in Table 1. The paint sludge was obtained from a motor manufacturer and ashed at a temperature of 800 ^oC for half an hour before analysis.

Table 1: Chemical composition of the raw materials used in this investigation (%m/m)

Compound	Sand	Waste Gypsum	Ash	Limestone 1	Limestone 2
SiO_2	93.5	6.3	8.2	6.2	18.9
Al_2O_3	2.0	0.5	17.4	1.0	2.3
Fe_2O_3	1.3	0.4	2.5	0.5	1.3
Mn_2O_3	0.0	0.1	0.2	0.7	0.1
TiO_2	0.3	0.1	55.1	<0.1	0.1
CaO	0.1	31.7	1.5	47.9	42.3
MgO	0.0	0.5	0.7	2.7	1.1
P_2O_5	0.0	0.1	12.6	0.2	0.0
SO_3	0.0	40.9	0.2	0.0	0.1
Cl	<0.1	<0.1	<0.1	<0.1	<0.1
K_2O	0.1	0.0	0.1	0.5	0.3
Na_2O	0.2	0.0	1.2	0.1	0.1
LOI	1.4	19.6	0.0	40.6	34.3
Total	98.8	100.2	99.7	100.4	100.9

All the materials used in this investigation were dry ground for three minutes in a laboratory ring mill before any mixing of the individual components for each raw meal was done. Initially a basic raw mix without any waste material was made from two standard limestones usually employed in the manufacturing of cement clinker. Furthermore, three different raw mixes that contained various amounts of waste material were designed that all had the same lime saturation factor (LSF) value of 95. The level of ash in the raw materials was chosen to conform to usual levels of ash incorporation from coal in the clinker under normal operating conditions (typically 1 to 3% by mass). It is common to use sulphur and phosphorus containing materials as fluxes and/or mineralizers for Portland clinker production in the process, and that is why the waste gypsum (a phosphogypsum

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from the fertiliser industry) was also incorporated into the clinker raw meal mixes. It can be observed from the results tabulated in Table I that the paint sludge ash contains a high amount of P_2O_5 that can act as a flux/mineralizer. The compositions of the initial raw mixes are summarised in Table 2.

Table 2: Composition of the initial raw meals compiled in this investigation (%)

Parameter	Basic Raw Mix	Raw Mix 1	Raw Mix 2	Raw Mix 3
LSF	88.0	95.0	95.0	95.0
SR	4.69	2.25	3.50	3.75
Limestone 1	20.1	79.8	31.5	46.5
Limestone 2	79.9	9.2	62.2	49.8
Sand	-	7.0	-	2.7
Ash	-	4.0	1.0	1.0
Waste gypsum	-	-	5.3	-
Target FCaO	1.5	1.5	1.5	1.5

A total mass of 1 kg of all the components of each raw meal were mixed together in the dry state in a Hobart mixer for 5 minutes before the onset of burnability tests. Once a raw mix has been constituted, burnability tests were performed according to the F.L. Schmidt methodology [19]. Each raw meal mixture was wetted with just enough water to give it a suitable consistency to be compacted into nodules of approximately 20-25 mm diameter. These nodules were dried at 105^{o}C in an oven for 24 hours to remove any free moisture and then stored in a dessicator until used. Subsequent to this, the different nodules were calcined at 1000^{o}C for half an hour before being clinkered at different temperatures for another hour. The different clinkering temperatures used for each of the raw mixes are given in Table 3.

Table 3: Clinkering temperatures used for the raw mixes investigated (^{o}C)

Basic Raw Meal	Raw Meal 1	Raw Meal 2	Raw Meal 3
1300	1250	1200	1250
1350	1300	1250	1300
1400	1350	1300	1350
1450	1400	1350	1400
1500	1450	1400	1450
1550	1500	1450	1500

After clinkering, the nodules were rapidly cooled in air and analysed for their free lime content according to the standard ASTM method utilising ethylene glycol extraction [20]. The remaining free lime in each case was considered as an indication of the burnability of the particular raw mix. As free lime contents in clinker normally vary between 0-3%, the aim was to produce clinkers which conform to these limits.

Subsequent to the free lime values obtained with the first trial mixes, further tests were conducted on two of the initial raw mixes, namely 2 and 3, containing waste materials in an effort to optimise their burnability. Although a very high final free lime value was obtained for the basic raw material, no further

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efforts were made to refine this mixture. Since ash incorporated into the clinker due to normal firing of the kiln by coal is approximately 1-3%, it was decided to choose the two raw meals containing 1% ash substitution as the mixes for optimisation. To achieve this aim, the LSF value was varied among the two raw mixes containing the same amount of paint wastes ash. The compositions of the different raw meals evaluated are shown in Table 4. Other approaches to optimise the burnability of the chosen clinker, included a third trial run in which the silica ratio as well as the amount of waste material used in one of the raw mixes were varied. This can be seen from raw mix compositions summarised in Table 5.

Table 4: Changes in the LSF value of raw meals 2 and 3 to optimise burnability

Parameter	Original RM 3	Modification 3A	Modification 3B	Original RM 2	Modification 2B
LSF	95.0	91.0	88.0	95.0	88.0
SR	3.75	3.75	3.80	3.50	3.50
Limestone 1	46.5	35.3	30.3	31.5	25.5
Limestone 2	49.8	62.1	67.4	62.2	55.2
Sand	2.7	1.6	1.3	-	-
Ash	1.0	1.0	1.0	1.0	1.0
Waste gypsum				5.3	18.3
Target FCaO	1.5	1.5	1.5	1.5	1.5

Table 5: Further changes to raw meal 3 to optimise its burnability

Parameter	Original RM 3	Modification 3C	Modification 3D
LSF	95.0	88.0	88.0
SR	3.75	4.0	4.0
Limestone 1	46.5	45.2	79.0
Limestone 2	49.8	50.0	10.1
Sand	2.7	3.8	9.4
Ash	1.0	1.0	1.5
Target FCaO	1.5	1.5	1.5

Once the materials resulting in the lowest amount of free lime after clinkering have been selected from the burnability trials, their grinding behaviour was investigated. For this purpose the different clinkers were dry ground in a Siebtechnik ring mill for one and three minutes respectively, before their Blaine surface areas were measured in the normal way [21].

In order to correlate the microstructural composition of the different clinkers produced with that usually encountered in normal clinker, XRD scans were recorded on a Siemens D5000 spectrometer. The XRD instrument used Cu ($K\alpha$) radiation and a voltage of 50 kV and a current of 20 mA. In addition to this, some of the materials were epoxy mounted, polished to a surface fineness of 1

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μm and etched with a 2% Nital solution for microscopic examinations on a Nikon optical microscope.

RESULTS AND DISCUSSION

The initial raw mixes given in Table 2 were designed with the following aims:

(a) To produce raw meals with similar production parameters as those typically used in cement plants.

(b) To optimise the use of waste material used to produce clinkers.

(c) To minimise the use of especially limestone 1 (primary, expensive limestone) in the production process.

(d) To optimise the burnability of the clinkers to obtain a suitable level of free lime in the final product.

The results of the burnability evaluation of the initial raw meals, as judged by the free lime contents of the clinker produced at different temperatures, are summarised in Table 6.

Table 6: Free lime contents (%) of the clinkers from the initial four raw mixes after heating (for 1hr) at various clinkering temperatures.

Temp. (^{o}C)	Basic Raw Meal	Raw Meal 1	Raw Meal 2	Raw Meal 3
1200	--	--	19.1	--
1250	31.2	19.2	16.7	24.2
1300	16.6	16.5	13.8	15.0
1350	12.8	15.2	12.0	12.5
1400	11.1	14.4	11.0	10.7
1450	9.2	12.8	8.9	9.9
1500	8.8	9.8	--	7.8
1550	6.1	--	--	--

From the values obtained it can be concluded that there is a significant difference between the burnabilities of the basic raw meal and three mixes containing waste material that were investigated, as well as in the burnabilities of the latter three amongst themselves. The final free lime content of the clinker manufactured from the basic raw meal under laboratory conditions varied significantly from what is experienced in the plant kiln and can be ascribed to different fineness of the raw meal, different temperature profile in the kiln and kiln operating conditions. No further effort was made to optimise the basic raw mix, since production material was available for intended further comparisons and concrete tests at a later stage. Raw meal 1 seems to have the poorest burnability, while the behaviour of No. 2 and 3 are fairly similar from about 1300^{o}C upwards. As can be expected, the presence of the waste gypsum improves the burnability of raw mix 2 compared to the other two because it can act as a mineraliser/fluxing agent in the clinkering process [22,23]. However, it has to be kept in mind that possible build-up problems could be experienced in real plant production scenarios if phosphogypsum is used in the raw meal.

Notwithstanding this, it was decided to try and optimise the burnability of raw meals 2 and 3. Raw mix 3 had a significantly better burnability than raw mix

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1 and a far more preferable consumption of especially limestone 1, although a lower amount of ash will be consumed in raw mix 3. The burnabilities of modifications A and B of raw meal 3 as well as B of raw meal 2 obtained after lowering the lime saturation factor of the basic mix, are presented in Table 7.

Table 7: Free lime contents (%) of the modified clinkers from the initial raw mix 2 and 3 after heating (for 1hr) at various clinkering temperatures

Temp. (^oC)	Raw Meal 3	Modification 3A	Modificati on 3B	Raw Meal 2	Modification 2B
1200	--	--	--	19.1	8.9
1250	24.2	23.7	13.0	16.7	6.9
1300	15.0	11.8	9.1	13.8	4.6
1350	12.5	6.9	8.5	12.0	3.0
1400	10.7	6.9	4.8	11.0	3.0
1450	9.9	6.4	3.7	8.9	2.9
1500	7.8	5.6	3.2	--	--

Although the target free lime value of 1.5% could not be reached with any of the modifications in the two original mixes, it is clear that in both cases the burnability of the raw mix was improved significantly. The strategy to reduce the LSF value of the initial raw meal to limit the possible amount of free lime remaining after clinkering, proved to be particularly successful in modification B of the two initial raw mixes.

In view of the encouraging results obtained, it was decided to try two more changes to modification B of raw mix no.3 in an effort to further increase its burnability. The burnabilities of modifications C and D of raw meal 3 obtained after changing the silica ratio and the amount of ash of the basic mix, are summarised in Table 8.

Table 8: Free lime contents (%) of the further modified clinkers from the initial raw mix 3 after heating (for 1 hour) at various clinkering temperatures

Temperature (^oC)	Raw Meal 3	Modification 3C	Modification 3D
1250	24.2	13.4	16.9
1300	15.0	9.4	14.6
1350	12.5	6.8	13.5
1400	10.7	5.1	11.0
1450	9.9	4.2	10.2
1500	7.8	3.2	8.7

Modification C in which the silica ratio was increased, yielded fairly similar results to those obtained in modification B. Modification C would probably increase the potential amount of alite present in the final clinker slightly, but it is doubtful whether the total amount of silicate phases that would determine the final 28 day strength would differ significantly between modifications B and C. Modification B would probably be the more economical to produce because of the high initial cost of limestone 1 compared to the rest of the constituents. Increasing the amount of ash added to the raw meal significantly impaired the burnability of the mix.

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In a further effort to distinguish the most suitable combination for continued strength and setting time evaluations, the grindability of some of the clinkers described above was compared. The behaviour of the clinker during grinding is directly related to the texture and structure of the crystal. Previous work [24] indicates that transition metal oxides, except for ZnO, generally have a favourable effect on clinker grindability. This can be ascribed to their effect on the formation of the liquid phase and the subsequent development and structure of the alite crystals. The results obtained after various grinding times are summarised in Table 9.

Table 9: Comparison of the grindability of various raw mixes and modifications, as measured by their respective Blaine surface areas (BSA) (in m^2/kg)

Mix Designation	Temp (^oC)	BSA (1 min)	BSA (3 min)
Basic raw mix	1500	200.4	384.9
Raw mix 2	1450	311.9	455.2
Modification 2B	1450	-	457.5
Raw mix 3	1500	267.4	488.3
Modification 3A	1500	292.1	386.4
Modification 3B	1500	285.2	326.6
Modification 3C	1500	340.5	382.9
Modification 3D	1500	357.7	487.1

Modification B of raw meal 3 has a slightly lower grindability than Modification C after three minutes of grinding. It is unclear why this is the case, as it cannot be ascribed to differences in free lime content or a significant difference in their phase microstructures, as was evident from microscopic examinations. The easy grindability of Modification D can largely be ascribed to its very high free lime content. The grindability of all the variations of raw mix 3, except B, after three minutes are similar to that of the basic raw meal, while the initial grindability after one minute are in all variations of raw meal 3 better compared to the basic raw meal composition's value. As far as raw mix 2 and its modification 2B are concerned, both clearly have a better grindability than the basic raw mix. Although it could be argued that this is due to the high free lime content in the clinker, this argument is not valid for raw meal modification 2 B. This latter clinker had similar free lime contents to modifications 3 B and 3 C of raw mix three and still had better grindability than both these two clinkers from a different raw mix. This evidence suggests that raw meal 2, and especially modification 2B, produce by nature a softer clinker than the others considered so far.

The XRD spectrum of the clinker produced from the basic raw meal is shown in Figure 1 and displays all the classical phases normally encountered in ordinary Portland cement clinker. In Figure 2 a comparison is made between the clinkers produced from raw meal 2 and 3, as well as the various modifications of no.3. Although the comparison is restricted mainly to the alite peak positions, it is very clear that the clinkers produced from raw meal no.3 and its various modifications are compositionally essentially identical. However, without trying to analyse it in too much detail, the clinker from raw meal no. 2 clearly displays a

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different microstructural composition. The micrographs of the clinkers produced from raw mixes 3 and its various modifications, displayed typically occurring angular alite phase crystals and rounded belite crystals well dispersed throughout the clinker matrix.

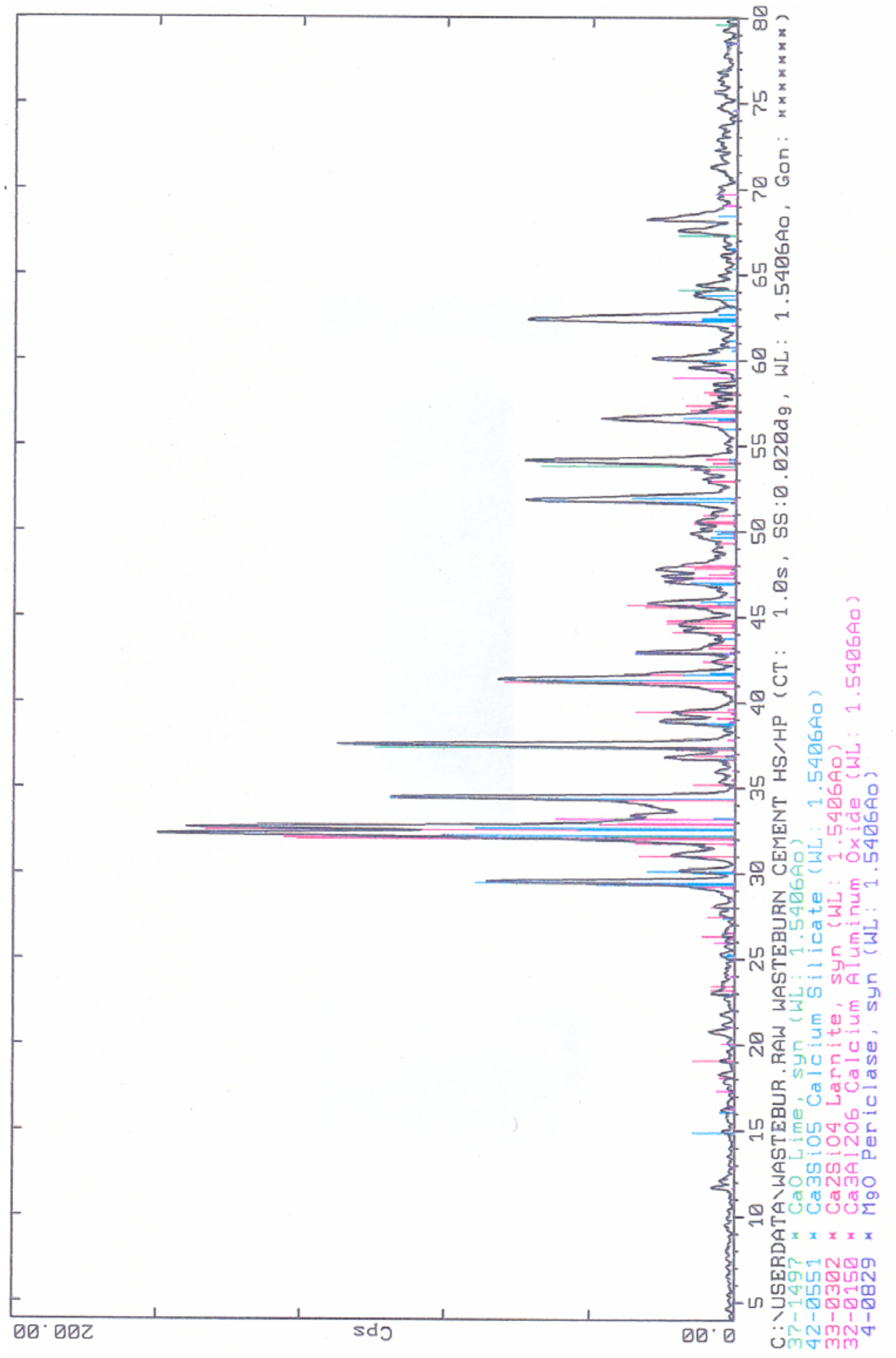

Figure 1 XRD scan of clinker produced from the basic raw mix.

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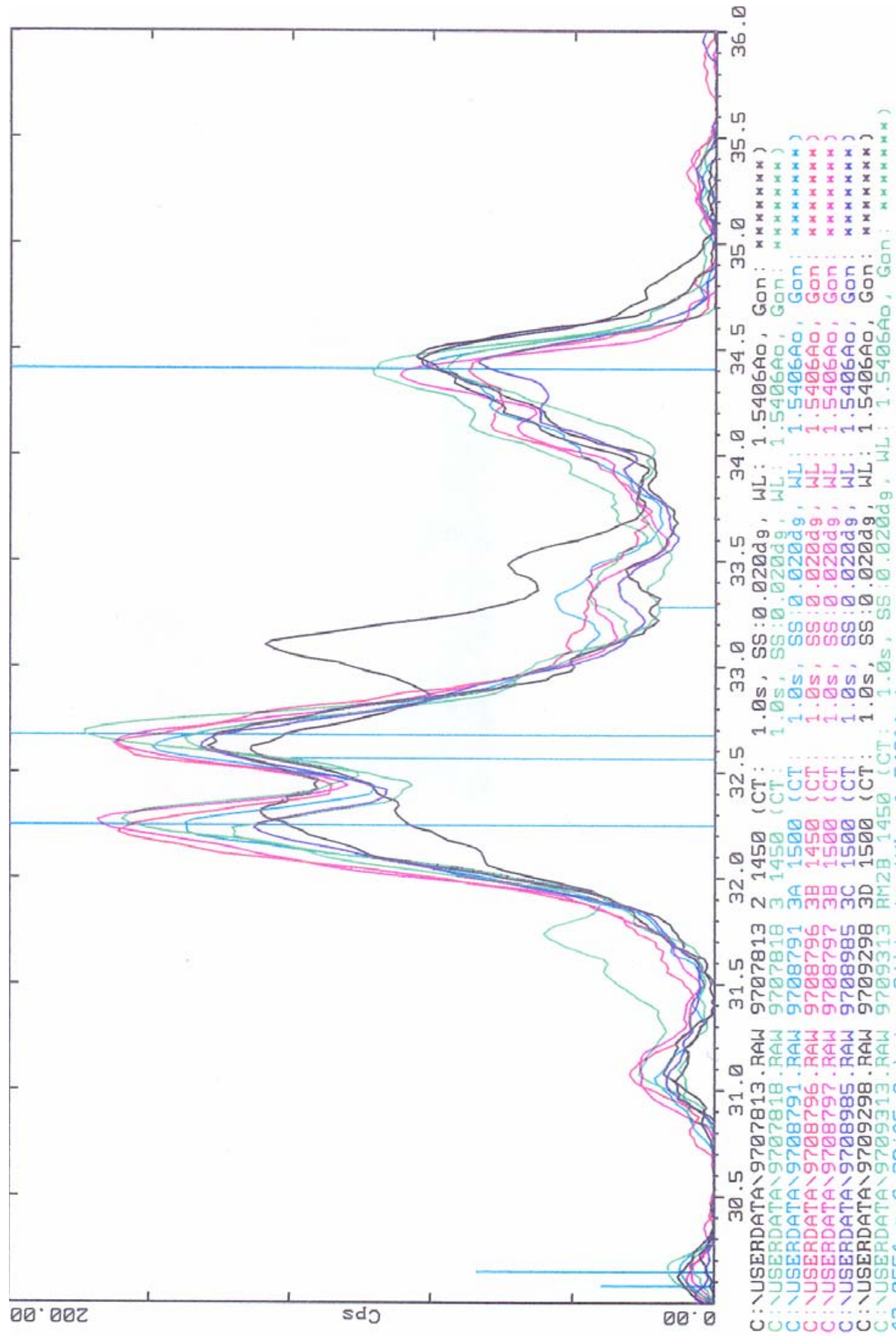

Figure 2. A comparison of the XRD spectra of the various clinkers produced from different raw meals at the main alite peak positions.

A major concern in any cement produced from waste material is its physical behaviour in concrete. This will be determined by both its microstructural components as well as its chemical composition. It entails an investigation of a completely different nature to the work being described in this summary and will be the focus of another paper.

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CONCLUSIONS

It was demonstrated that an OPC clinker could be produced that incorporated paint sludge ash, without compromising the burnability and microstructure of the baseline clinker made from a production raw mix. Grindability seems to be generally better in the clinkers containing waste materials and having modified compositions. From the results thus far it seems like modification B of raw meal 3 would be the most preferable one to select for further strength and setting time evaluations. Once the chemical compositions of each of the different combinations have been determined and compared with that of the production basic formulation, the setting times, strength development and concrete behaviour of modification B of raw meal 3 could be investigated to determine its suitability for application. If there are significant amounts of heavy metals from the paint wastes incorporated in the final clinker, there is a very real possibility that it might influence the final use of the cement in concrete applications.

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