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### Potential use of thermally desorbed soil as a partial cement replacement

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#### Abstract

*The industrial heritage of the UK has given rise to around 100,000 sites, being classified as contaminated. There are many different techniques that have recently been developed to remediate land. Thermal desorption is one of these techniques. Contaminants in the soil are volatilised, which are then removed by a thermal or catalytic oxidiser. The chemical and physical properties of the 'burnt' soil', termed thermally desorbed soil (TDS), have significantly changed but is typically still disposed of to landfill.*

*The use of supplementary cementing materials has become a central aspect of construction economics and environmental preservation. This study therefore investigated the potential use of TDS as a partial cement replacement material. Cement was replaced from 0% (as the control) to 30% TDS in 10% increments. The compressive strength of the mortar cubes was then determined at intervals of 7, 28 and 91 days. For a direct comparison, a well-established pozzolanic material, fly ash (FA) was tested throughout the programme.*

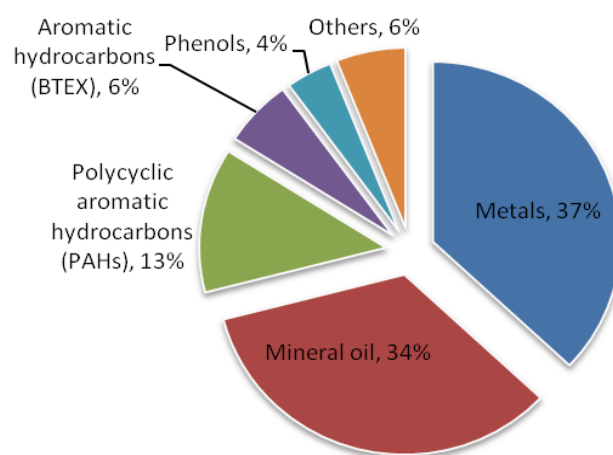
*Strength was indirectly related to replacement level, with the control initially (up to 7 days) gaining, and thereafter retaining, the highest degree of strength. However, after 7 days the rate of gain in strength was higher for the replacement mixes (FA and TDS) than the control. There was no significant strength difference between the FA and TDS mixes up to 20% replacement. Hence, based on these initial strength results, the performance of TDS as a partial cement replacement (up to 20%) was directly equivalent to that of FA.*

*Environmental benefits for the use of TDS as a partial cement replacement would be twofold; firstly, by using a waste material rather than disposing to landfill; and secondly by using less cement. This would result in less carbon dioxide (CO<sub>2</sub>) being released into the atmosphere during the cement manufacturing process, which is currently responsible for 7–10% of the global CO<sub>2</sub> emissions.*

# 1. INTRODUCTION

The planning policy statement 23 (PPS23) for government policies on land affected by contamination gives guidance on the use of Brownfield<sup>1</sup> land for development. Many existing Brownfields are currently causing damage to the natural environment. Typically, this is from harmful pollutants leaching from the soil, which have been trapped from past industrial activity, into the surrounding watercourse. As such, it is paramount that these sites are remediated to prevent such an occurrence. A contaminant can be considered as a compound present in soil at higher concentrations than would be expected, and that has the potential to cause harm to the environment as a result of the concentration (Starkings and Cromie, 2007). Xenobiotics encompass all compounds that are foreign to living organisms. Such compounds may be released into the environment accidentally or due to negligence from industrial, agricultural or domestic usage (Alexander, 1999).

Contaminants are usually classified as organic or inorganic. Organic contaminants are those of biological origin. The inorganic contaminants are considered to be of non-living, non-biological origin (Holleman and Wiberg, 2001). Inorganic contaminants can be classified by the elements or groups they contain and include metals and non-metals (Madsen, 2003). They can also be attributed to petroleum, batteries, paint/wood preservatives, leaded petroleum and agricultural dips. Some inorganic contaminants such as sulphides, sulphates and cyanides generally arise as by-products from manufacturing industries (Sarsby, 2000). Figure 1.1 present examples of the most common contaminants found in soils. Sites contaminated with polycyclic aromatic hydrocarbons (PAHs) over a century ago are still routinely found to contain high levels of these contaminants despite long-term weathering and reduction processes.



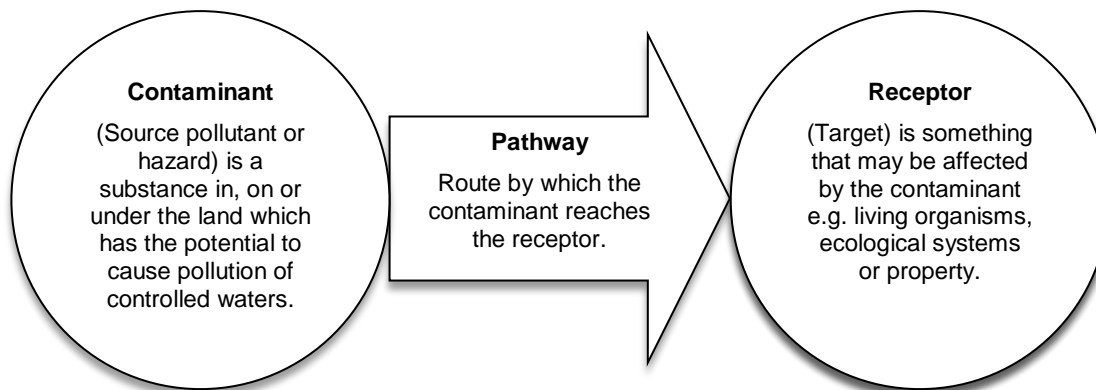
**Figure 1.1: Overview of contaminant types**

Remediation is initiated to guard human beings and their surroundings and allow the process of redevelopment to take place. Risk, in land contamination, results from three

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<sup>1</sup>The US Environmental Protection Agency gave in 1996 a definition of 'brownfield' as: "...an abandoned, idle or underused industrial or commercial property where expansion or redevelopment is complicated by real or perceived environmental contamination".

elements, namely: a contaminant, pathway and receptor, as illustrated in Figure 1.2. Land is believed to be contaminated and requires remediation if the three elements of the pollutant linkage are in place. Remediation looks to remove one of these elements or break the linkage between these elements to prevent further pollution (harm) from occurring.



**Figure 1.2: Pollutant linkage (Adapted from Environmental Protection Act, 1990)**

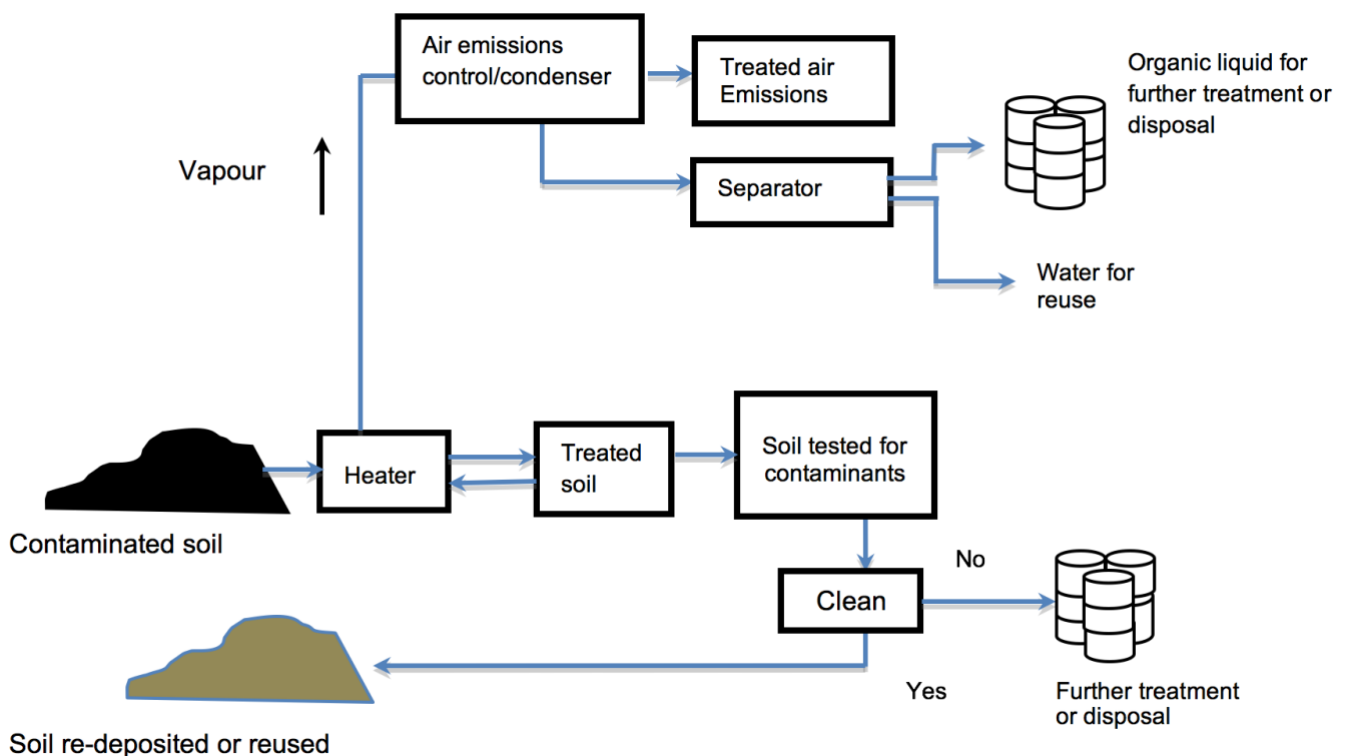
In the UK the choice of a remediation process is influenced by cost-effectiveness, speed of reclamation and flexibility (Beckett and Cairnery, 1993). There are several technologies that can be employed for land remediation. They can be described as chemical, physical, solidification/stabilisation, thermal and biological. The technologies can be undertaken either *in-situ* or *ex-situ*. Table 1.1 shows the classification of the most common remediation options used in the UK.

**Table 1.1: Main remediation technologies used in the UK (Nathaniel *et al.*, 2002)**

Technology	Class	Application	Medium
Excavation & disposal	Civil Engineering	<i>Ex-situ</i>	Soil, water vapour
Pump and treat	Physical	<i>Ex-situ</i>	Water,
Air sparging	Physical	<i>In-situ</i>	Water
Soil washing	Physical	<i>Ex-situ</i>	Soil
Soil vapour extraction	Physical	<i>In-situ</i>	Soil
Windrows	Biological	<i>Ex-situ</i>	Soil
Biopiles	Biological	<i>Ex-situ</i>	Soil
Thermal desorption	Thermal	<i>Ex-situ</i>	Soil
Vitrification	Thermal	<i>In-situ</i>	Soil
Incineration	Thermal	<i>Ex-situ</i>	Water vapour
Capping	Civil Engineering	<i>In-situ</i>	Soil
Vertical barriers	Civil Engineering	<i>In-situ</i>	Water, vapour
Bioslurping	Biological	<i>In-situ</i>	Water
Biosparging	Biological	<i>In-situ</i>	Water
Oxidation	Chemical	<i>In-situ</i>	Soil
Reduction	Chemical	<i>In-situ</i>	Soil
Natural attenuation	Biological/Chemical/Physical	<i>In-situ</i>	Water

Thermal desorption is a technique that uses direct or indirect heat to destroy contaminants by exposing the contaminated media to high temperatures (Bouwer and Zehnder, 1993). This process uses burners to provide heat to deplete the levels of contaminants within the soil. Contaminants are heated to temperatures ranging between 500 and 650 °C to volatilize and separate them from the soil.

The vaporised contaminants are then passed through a vapour system to destroy the contaminated gases before they are emitted into the atmosphere, as illustrated in Figure 1.3. Heat can be applied by radiation or by convection from direct contact with combustion gases and can also be indirectly applied by heating the outside of the cylinder (TR-2090-ENV, 1998). It is a proven sustainable technology and has a firmly defined outcome for both organic and inorganic contaminants (Starkings and Cromie, 2007). Thermal desorption is considered to be an appropriate solution for sites where a complex array of contamination is present, such as gasworks and chemical plants. The thermal process changes the structure of the soil matrix by destroying the organic compounds, leaving a residual soil with a consistency of ash (Allen, 2009). The resultant remediated soil is either disposed of to landfill or used as a fill material, depending on how successful the remediation process has been.



**Figure 1.3: Thermal desorption process (EPA, 2004)**

When used as fill material, the *in-situ* strength property of the TDS has been noted to increase with respect to time, hence indicating some form of cementitious or pozzolanic action naturally emanating from the burnt soil. Thus, the research work detailed in this paper considers the potential use of TDS as a partial cement replacement. The advantages being the reuse of a waste material together with a reduction in the amount of cement required. The resulting outcomes being a saving in landfill space and cost, together with a reduction in CO<sub>2</sub> emissions from manufacturing less cement.

## 2. LITERATURE REVIEW

The literature review is presented in two main sections. The first section contains a general information on cement and the second section concentrates on pozzolans, in particular FA.

### 2.1 Cement

Cement is a material with adhesive and cohesive properties capable of bonding mineral fragments (sand, bricks, stone, etc) together. It is capable of reacting with water to give a hard strong mass. The main cement constituents are calcium carbonate (from chalk or limestone); silica and alumina (both from clay/shale). Cement is manufactured by heating limestone and clay together to form clinker rich in calcium silicates. This is ground to fine powder with a small proportion of gypsum (calcium sulphates), which controls the rate of setting when the cement is mixed with water.

Table 2.1 gives an analysis of the sources of CO<sub>2</sub> emissions associated with cement manufacture. One of the main ways to reduce CO<sub>2</sub> emissions, is to reduce the amount of cement manufactured by blending it with other binding materials, such as pozzolans. Table 2.2 demonstrate the range of blended cements used in the UK.

**Table 2.1: CO<sub>2</sub> emissions associated with the production of one tonne of PC (Adapted from: ICT, 2007)**

Source	Indicative CO <sub>2</sub> emitted (kg)	Comment
Chemical decomposition (breakdown of limestone)	800–900	The major source of CO <sub>2</sub> is intrinsically unavoidable
Fuel	350	Use of waste as fuel can benefit sustainability
Electricity	80	The CO <sub>2</sub> is normally emitted off-site at a power station
Total	1,330	

**Table 2.2 Cement types and clinker ratio (Price, 2009)**

Cement type	Second main constituent	Minimum clinker (%)	Maximum cement/clinker
CEMI	–	95	1.05
CEM II/A-S	Slag	80	1.25
CEM II/B-S	Slag	65	1.54
CEM II/A-V	Fly ash	80	1.25
CEM II/B-V	Fly ash	65	1.54
CEM II/A-L	Limestone	80	1.25
CEM II/A-D	Silica fume	90	1.11
CEM IV/B	Fly ash	64	1.56
CEM III/A	Slag	64	1.56
CEM III/B	Slag	20	5.00

## 2.2 Pozzolans

The term pozzolan refers to materials that react with calcium hydroxide (CH), in the presence of water, to form hydrated products with binding properties (Massazza and Costa, 1979). Natural pozzolans include volcanic ash, diatomaceous earth, metakaolin (calcined clay) and opaline shade. Artificial pozzolans include FA – also known as pulverized fuel ash (PFA), brick dust, calcined kaolin, rice husk ash (RHA), silica fume, ground granulated blast furnace slag (GGBS or slag) and certain types of metallurgical slags. Pozzolans comprise of silica in a reactive state, being in the form of siliceous and aluminous materials.

FA is one of the most commonly used pozzolans. It is a coal by-product generated by the combustion process that occurs in coal-fired plants. Coal is ground and blown with air into a combustion chamber where it instantaneously burns, producing heat and creating a molten mineral residue (Roy *et al.*, 1981). After cooling the molten residue hardens and becomes ash. The ash is a complex material consisting of powdery spherical particles that are a heterogeneous combination of amorphous and crystalline phases (Karim *et al.*, 2011). FA consists of crystalline minerals (namely: quartz, mullite, cristobalite, magnetite, maghmite and hematite) and non-crystalline (amorphous) glass (Ward and French, 2005).

Interest in the use of FA as a cement replacement began in the late 1940s. FA was selected for use in the construction of the Lednock, Clatworthy and Lubreoch dams in Scotland, UK (Allen, 1959). For example, the construction of Lednock dam involved 62,500 m<sup>3</sup> of concrete and the use of FA saved 3,000 tons of PC.

About 10,000 million tonnes of FA is produced in the UK every year and half of this amount is used in the construction industry (Khatib, 2009). The utilisation of FA is due to environmental, economic and technical considerations (Fu *et al.*, 2002; Worrell *et al.*, 2002). Environmentally, the use of FA as a pozzolanic material in the manufacture of cement, contributes to the reduction of about 25 million tonnes of CO<sub>2</sub> emissions per annum (Ahmaruzzaman, 2010). Economically, the utilisation of the FA has the following financial returns (Environmental Agency, 2010):

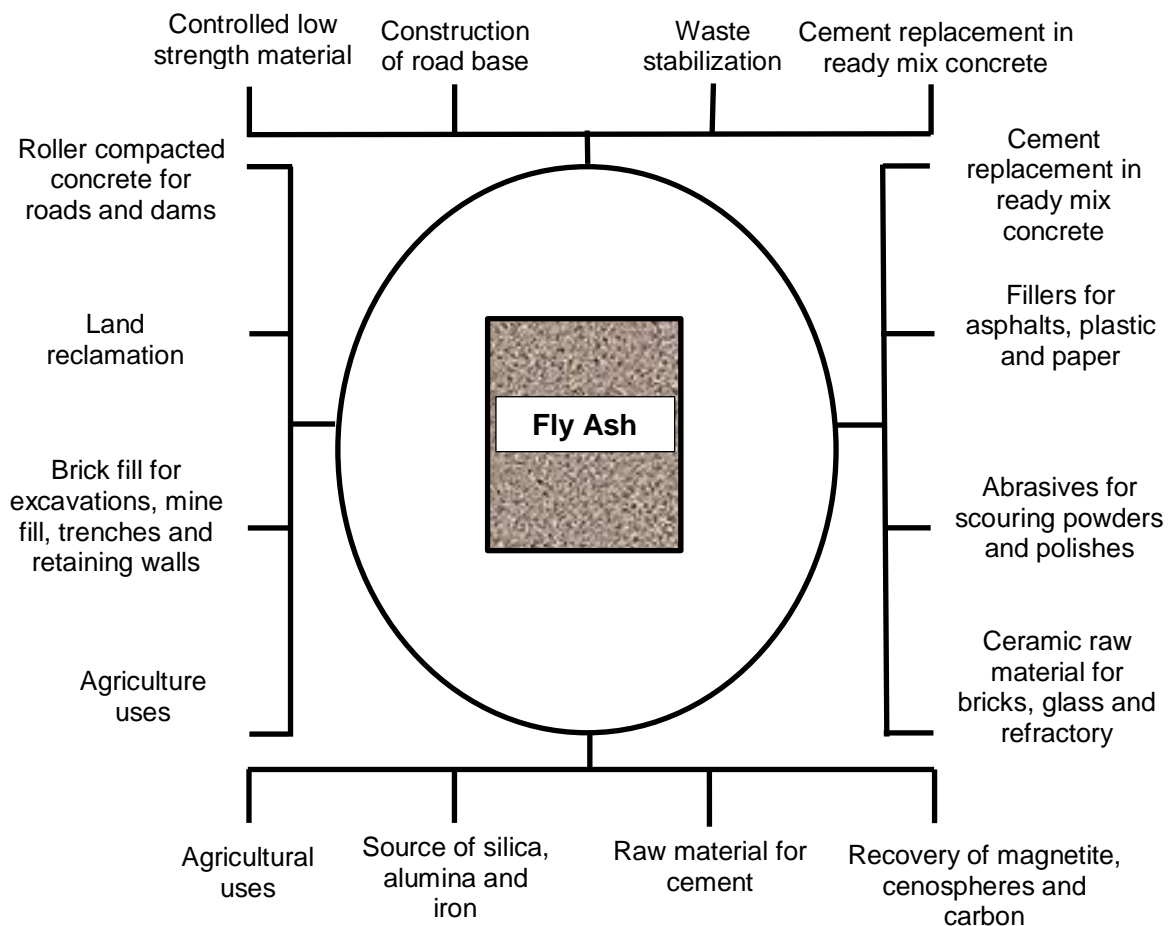
- It saves the power industry £5 million each year, largely due to the reduction in landfill charges which would be associated with its disposal.
- It creates markets (as illustrated in Fig. 2.1) worth over £8.5 million a year.

Also in respect to technical consideration research has shown that the use of FA has a large number of positive effects (including factors such as workability, drying shrinkage and durability) on the fresh and hardened states of mortar/concrete.

## 2.3 Summary of literature

In order to confront the problems of climate change it is imperative that CO<sub>2</sub> emissions from the cement industry are reduced and waste streams are minimised. Partially replacing cement with a pozzolanic material (such as FA) to form a blended cement is a very positive development in the cement industry's efforts to achieve sustainability.

The rest of this paper is directed towards investigating the potential use of TDS as a partial cement replacement as a new pozzolanic (or cementitious) material. Throughout the testing programme FA was tested alongside TDS so that a direct comparison could be made with that of a well-established pozzolan.



**Figure 2.1 Possible use of FA based on properties (Adapted from Wang and Wu, 2006)**

### 3. MATERIALS

The TDS used in this research programme was sourced from the former Avenue Coking Works Site. The Avenue Site is located in Chesterfield, Derbyshire, UK – National Grid Ref 438994,367888. The general solid geology of the area is composed of Middle and Lower Carboniferous coal measure, which consists of inter-bedded mudstone, siltstone, sand stone, shale and coals (EMDA, 2001). The site is 98 hectares and was used for 36 years for coking and chemical works. At full capacity the coking works employed 800 staff and carbonised 2,175 tonnes of coal a day; producing approximately 1,400 tonnes of smokeless fuel, 65 tonnes of sulphuric acid, 35 tonnes of ammonium sulphate, 250 tonnes of tar and 20,000 gallons of crude benzole. Prior to the coking and chemical works, it was used as a coal mining and iron works site. It also received waste from other National Coal Board sites in the region. It is a prominent site within the region and also nationally within the remediation sector as it was dubbed, in the late 1990s, as one of the most

contaminated site in Europe. The site is contaminated with a complex array of chemicals, such as sulphates, creosote, blended fuel wastes, benzol, tars, asbestos and spent oxides.

The complex myriad of contamination and the inconsistent underlying ground conditions on site gave an indication that there was no single treatment technology that was able to remediate the soil. The remediation trial programme in 2001 was based on the use of many techniques to assess the most suitable technologies. In October, 2010 the Avenue Site commenced its full remediation works. The majority of the soil (300,000m<sup>3</sup>) was treated by thermal desorption, followed by bioremediation (75,000m<sup>3</sup>) and soil washing (50,000m<sup>3</sup>). It was the soil from the thermal desorption plant that was used in this research investigation. The soil was double bagged using shovels and the tops loosely tied using tie wraps. The bags were then transported to Leeds Beckett University and kept cool and in the dark in accordance with BS7755-2.6 (1994).

The other constituents of the mix consisted of a common base of PC, general purpose sand, hydrated (HL2 building) lime and tap drinking water. The type of PC used in this testing programme was Procem CEM I 52.5N from Lafarge Cement. It also has consistent strength conforming to the BS EN 197-1 (2000) requirements. The FA was supplied by Drax Power Station, North Yorkshire, UK.

#### **4. RESEARCH METHOD**

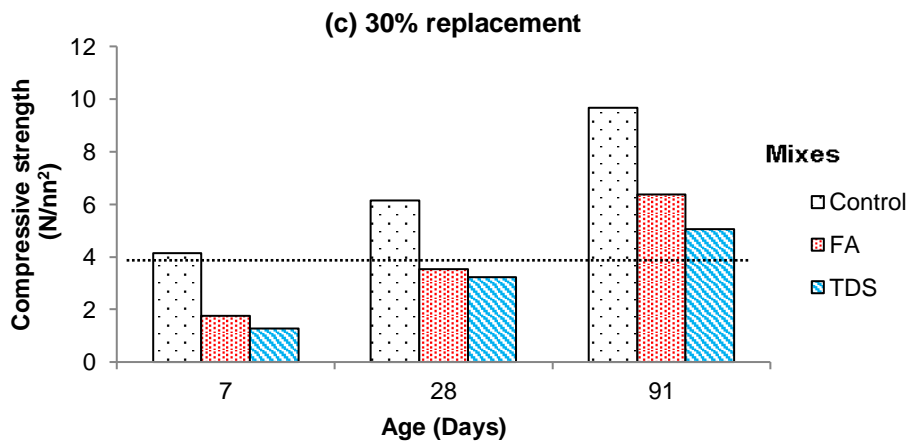
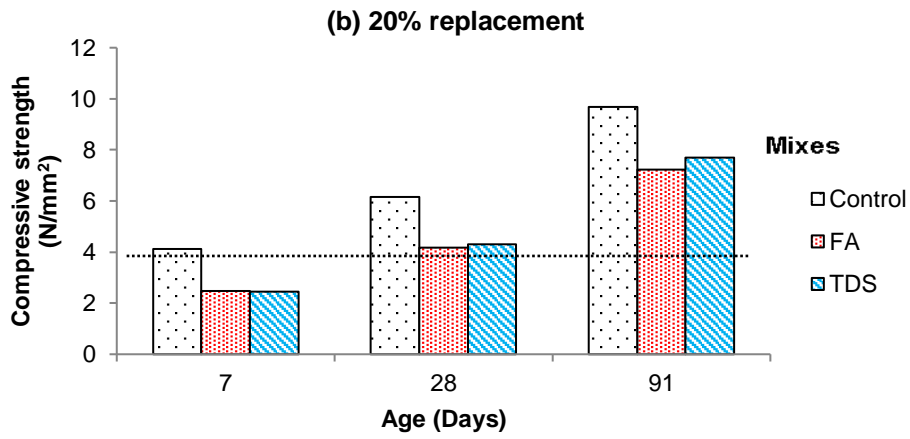
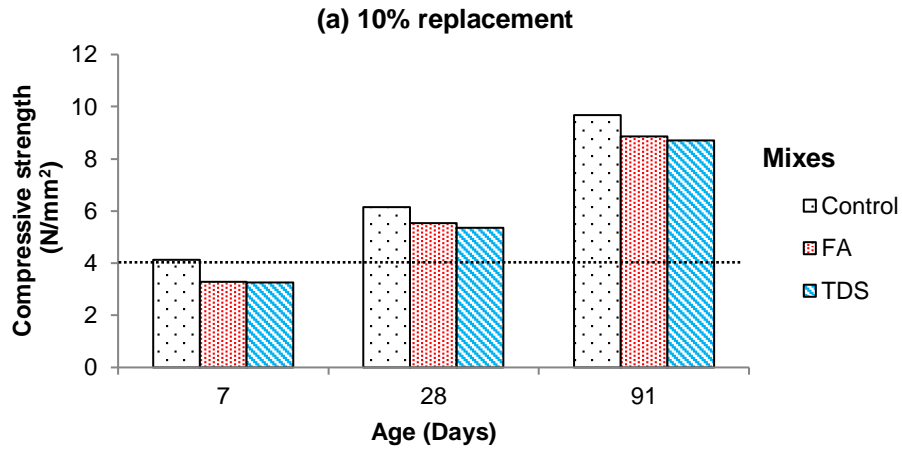
A laboratory based experimental programme was undertaken to evaluate the effects of partially replacing cement in mortar with TDS (and FA). Preparation and storage of the specimens was carried out in accordance with BS EN 1015-11 (1999). The percentage of cement replacement with TDS (and FA) ranged from 0–30% in increments of 10% by weight. Replacement by weight rather than by volume is favoured as it provides better accuracy and avoids bulking problems (The Concrete Centre, 2011). For control purposes a control mix with 100% PC mortar (i.e. 0% cement replacement) was used throughout the testing programme. Each mix was repeated three times to ensure replicability.

Mortar samples were prepared at room temperature. The water/binder (w/b) ratio of 0.6 was established from trial mixes based on the texture of the materials and the volume of the mix, as well as the workability of the mortar. The w/b ratio was constant for all the mixes. The sand/binder ratio (s/b), by weight, was equal to 10.6 and was maintained constant throughout the experiment.

#### **5. RESULTS**

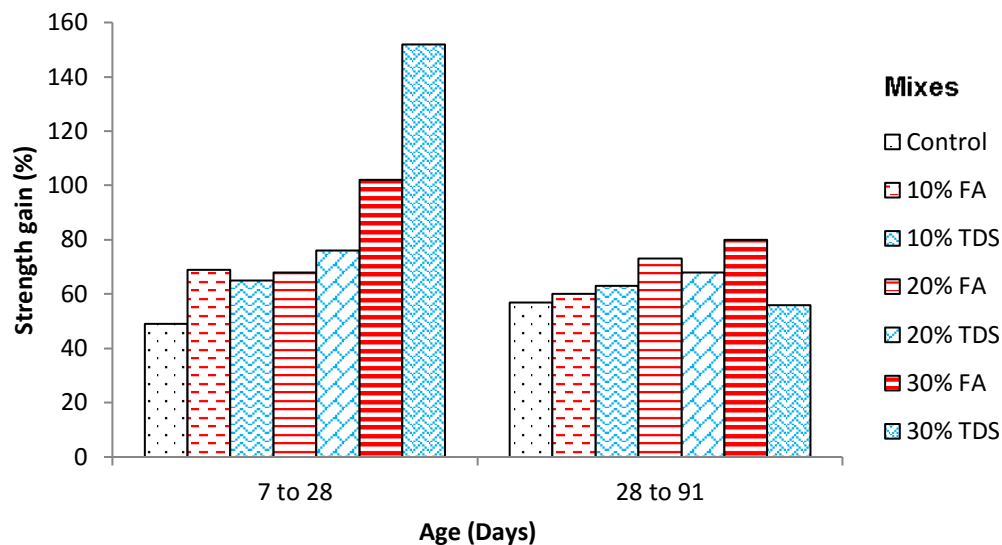
Figure 5.1(a–b) shows the mean performance of the 10, 20 and 30% FA and TDS mortar cube samples at set curing durations. The dashed line of the figure represents the minimum strength requirement of 4 N/mm<sup>2</sup> as specified by BS EN1996-1-1 (2005) for category (iii) masonry mortars.





**Figure 5.1 Replacement mortars vs control**

The rate in compressive strength gain for the control and cement replacement mixes (both FA and TDS) from 7 to 28 days and 28 to 91 days is shown in Figure 5.2.



**Figure 5.2: Compressive strength gain**

## 6. DISCUSSION

From Figure 5.1 it can be seen that the strength of the replacement mixes trailed the strength of the control. The strength was indirectly related to replacement level, i.e. as replacement material increased less strength was obtained. At 10% replacement, there were no significant difference between the strength of the TDS and FA. At 20%, TDS and FA samples were again directly comparable up to 28 days; thereafter, TDS gained slightly more strength, being 6.5% stronger at 91 days than FA. However, at 30% replacement the inverse was true, with FA being slightly stronger than TDS.

At 7 days the mean strength of the control was 4.13 N/mm<sup>2</sup>, which just met the minimum strength requirement of 4 N/mm<sup>2</sup> (dashed lines on Fig. 5.1). However, none of the replacement samples (TDS and FA) met this requirement at 7 days. The strength of the 10 and 20% replacement samples was just over 5 N/mm<sup>2</sup> at 28 days, which now met the minimum requirement. At 30% replacement both TDS and FA failed to meet the specified 4 N/mm<sup>2</sup> at 28 days but exceed this minimum value at 91 days.

Up to 7 days the control had the greatest rate of strength gain; the trend then followed replacement level. This would be expected as the pozzolanic action of the replacement mixes would not be evident until after this timescale (Neville, 2011). Between 7 and 28 days all the TDS and FA replacement mixes (10–30%) had a higher strength gain over that of the control (Fig. 5.2). This was particularly true for the 30% replacement mixes, which was probably due to the higher percentage of pozzolanic material. This confirms data published by previous researchers (e.g. Atis *et al.*, 2003; Chindaprasit *et al.*, 2004) who also observed

that the pozzolanic reaction is more apparent from 7 days. The actual strength, however, remained lower than the control.

Between 28 and 91 days, apart from the TDS at 30%, the replacement mixes had higher strength gains than the control (Fig. 5.2). Normally the strength of the control mix reaches a plateau from around 28 days. For the 10% replacement samples the TDS and FA mixes had comparable strength gains around 60%. At 20% replacement level the strength gains were again similar being around 70% for both replacement materials. However, at 30% replacement the FA mix had superior strength gains to the TDS mix, which does not fit the recognised trend, hence further testing would be required for confirmation.

In general, the higher the amount of replacement material the greater the strength gain after 7 days. However, overall the strength is somewhat compromised by the initial strength (up to 7 days) being indirectly proportional to replacement level. In practice, pozzolanic materials strength gains are noticeable between 7 and 28 days (Kiattikomol *et al.*, 2001; Chindaprasirt *et al.*, 2004). It was found that the TDS samples performed in this way. Up to 20% replacement the TDS samples directly matched the compressive strength of the FA samples when cured up to 91 days.

## 7. CONCLUSIONS & FURTHER WORK

TDS and FA mortars exhibited inferior compressive strength to the control PC mortar at 7, 28 and 91 days of curing. Up to 20% replacement level there was no real strength differential to report between TDS and FA – both meeting the strength requirement of category (iii) mortars at 28 days. However, at 30% replacement level TDS strength lagged behind FA.

The improved TDS properties could be attributed to the burning of the original geological materials (clay and shale). Also, the heating of contaminants such as lime solids, burnt shale, clay, clinker and lime waste contributed to the cementitious properties of the soil.

The use of TDS as a partial cement replacement would reduce the embodied CO<sub>2</sub> in a mortar mix. For example, if 20% cement is replaced this would result in the reduction of about 188 kg of CO<sub>2</sub> per tonne of PC not being released into the atmosphere. Also, there will be a cost saving to be gained in terms of the reuse of TDS, i.e. not disposing it as a waste material.

Data will soon be published to demonstrate the:

- Long-term strength of TDS mortar samples, i.e. up to 654 days.
- Influence TDS fineness has on the overall strength and workability.
- Flexural strength of TDS mortar samples.
- Drying shrinkage of TDS mortar samples.
- Durability of TDS mortar samples in respect to freeze/thaw damage and sulphate resistance.
- Chemical and mineralogy profiles of TDS by X-ray diffraction (XRD) and X-ray fluorescence (XRF) respectively.
- Potential use of TDS in concrete.

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