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THE USE OF GLYCEROL AND COOKING OIL IN MASONRY UNIT PRODUCTION

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ABSTRACT

This paper presents an investigation into the development of a novel glycerol bound masonry unit and the use of multi-parameter mathematical modelling technique in evaluating the possibility to reduce the amount of sample produced with a comparable result obtained. Initially, an experimental optimisation was carried out to identify the best performance sample in term of compressive strength. The binder used for this stage is the blend of clean cooking oil and pure glycerol incorporating with secondary aggregates include incinerator bottom ash (IBA) and pulverised fuel ash (PFA). Additional samples were made using natural aggregates and waste binders (waste cooking oil and waste glycerol) to evaluate their performance in relation to masonry products found in the UK i.e. compressive strength and water absorption properties. These properties are good indicators of overall performance of masonry units. In addition, modelling techniques were also used to evaluate the laboratory testing strategy to suggest the reduction in number of samples being produced in future experimental studies. Results from the study demonstrated that the novel masonry units could be produced with properties that were at least equivalent to those of currently used in the UK and modelling technique could reduce up to 90% of sample for the problem with 3 parameters.

KEYWORDS: masonry, glycerol, cooking oil, hardening, optimisation, response surface building.

1. INTRODUCTION

In previous studies, it has been shown that bitumen (Forth *et al.,* 2004, 2006, 2010a and 2010b; Vu *et al.,* 2014) and more recently waste vegetable oil (Forth and Zoorob, 2006; Zoorob *et al.,* 2006; Heaton *et al.,* 2012) could be used as a binder for masonry units. In the latter work, a mix was developed using 5 % waste vegetable oil with limestone aggregates; the mix was moulded, compacted at 4 MPa and cured at 160 ºC for 12 to 48 h. Compressive strengths of between 14.2 MPa and 30.7 MPa were obtained. In that study (Zoorob *et al.,* 2006), limestone – a natural aggregate which is excavated from a quarry and is similar to those aggregates used for concrete mixes - was used. However, when waste aggregates (i.e. bottom ash, IBA) were substituted for the limestone aggregates, the binder proportion increased to 12 % (Heaton *et al.,* 2012). From an environmental and economic perspective this was considered too high and an alternative method or a more efficient way of distributing the oil within the matrix was required. Glycerol, which is more widely available (as a by-product of the bio-fuel industry) and is an order of magnitude less expensive than typical vegetable oils was therefore considered as a partial replacement for the vegetable oil binder. It was also hypothesised that the glycerol would help to distribute the oil around the system and hence reduce the required oil content. Changes in EU Directive (EC, 2013) in 2013 limited the use of biofuel from crops in transport by 2020 should not exceed 5%. Therefore, less biofuel will be produced hence lower amount of glycerol generated. This might make the application of glycerol in producing masonry unit less attractive. However, energy saving properties of the glycerol bound materials might be the main reason to consider.

This investigation used a blend of waste glycerol and waste cooking oil as a binder, with IBA and a waste filler material, to produce a masonry product with the levels of performance that were at least equal to clay bricks or concrete blocks currently used in the UK. Curing temperature was also identified as an important parameter to reduce. The firing of clay bricks normally takes between 24 to 72 hours and the highest temperatures may be higher than 1000 ^{o}C, resulting in an energy consumption of 1.84-2.8 kJ/kg and the emission of 184-244 kg of CO_2 per tonne of bricks (Forth and Shaw, 2013). Therefore, utilising curing temperatures of less than 200 ^{o}C in this investigation will significant reduce energy consumption and CO_2 emissions.

Initial studies were carried out using clean cooking oil and pure glycerol. Latterly, the investigation replaced the pure binders with equivalent waste binders. An evaluation study was therefore carried out to compare the performance of samples made from pure binders and waste binders; a sample made from pure binders and natural sand and gravel was also investigated to act as a control sample.

Previously, an investigation carried out by the authors showed that it was possible to optimise the bitumen binder of a masonry unit (Bitublock) using mathematical modelling techniques (Forth *et al.,* 2010a and 2010b). The modelling showed that the number of experimental samples required to optimise the binder could be reduced by 50 % (Forth *et al.,* 2010b). However, the experimental and modelling optimisation was simplified, being limited to only 2 parameters. Evidence (Vu, 2012) suggested that with further manipulation of the modelling theory it should be possible to reduce the number of experimental samples required beyond that already achieved previously (Forth *et al.,* 2010b) and at the same time increase the number of parameters from 2 to 3.

This investigation therefore aims to develop the use of waste glycerol as an alternative, sustainable organic binder to current traditional binder materials (i.e. cement, clay). The glycerol will either act independently or be blended with waste cooking oil. In addition, the research aims to extend the application of current optimisation modelling theory and as a consequence further optimise the copious laboratory work which is traditionally required by such investigations, an aim in-line with the sustainability nature of this research.

2. MATERIALS AND METHODS

2.1. Materials

2.1.1. Natural Aggregates

Aggregates used to produce the Control samples were natural sand (<5 mm) and gravel (5-10 mm) collected from Tarmac Road-stone, Wolverhampton, West Midlands, UK. The proportion of sand to gravel was 70% and 30%, respectively. This proportion was used as it was similar to the ratio of fine to coarse particle sizes found in incinerator bottom ash (see below).

2.1.2. Incinerator bottom ash

Incinerator bottom ash (IBA) used in this study was collected from Eastcroft Energy from Waste Facility - Waste Recycling Group (WRG) –Nottingham, UK. The collected IBA was dried and processed to the following particle sizes; 5 – 10 mm and < 5 mm. The mixing ratio of these two aggregate types was 0.3:0.7. This mixing ratio was used throughout the research project to maintain the consistency of the mix.

Table 1. Typical chemical composition of IBA and PFA

Constituents	**Unit**	**IBA**	**PFA**
Silicon Dioxide (SiO_2)	%	54.2	52.07
Aluminium Oxide (Al_2O_3)	%	18.1	34.42
Calcium Oxide (CaO)	%	10.4	4.18
Ferrous Oxide (Fe_2O_3)	%	3.0	3.54
Sodium Oxide (Na_2O)	%	3.0	0.09
LOI (at 550°C)	%	3.0	-
Chloride as Cl	%	1.8	-
Magnesium Oxide (MgO)	%	1.5	1.11
Potassium Oxide (K_2O)	%	1.0	0.52
Combustible matter	%	1.0	-
Sulphur Trioxide (SO_3)	%	0.8	1.39
Titanium as TiO_2	%	0.5	1.88
Zinc as ZnO	%	0.4	-
Copper as CuO	%	0.3	-
Lead as PbO	%	0.2	-
Manganese as MnO	%	0.1	-
Phosphorus Pentoxide (P_2O_5)	%	-	1.42
As, Cd, Cr, Hg, Ni, Sn	%	Trace	-

2.1.3. Pulverised fuel ash

Pulverised fuel ash (PFA) was used as a filler material in the control samples and the samples with IBA. It was collected from FerryBridge ‘C’ Power Station – West Yorkshire. The specification for PFA complies with the British Standard EN 450 Type S (BSI, 2005) with more than 80% of the particles being less than 45microns. Typical properties of the aggregates and filler used in this investigation are shown in Table 2. Figure 1 showed the gradation of the aggregates used in the investigation. Table 1 showed the typical chemical composition of PFA.

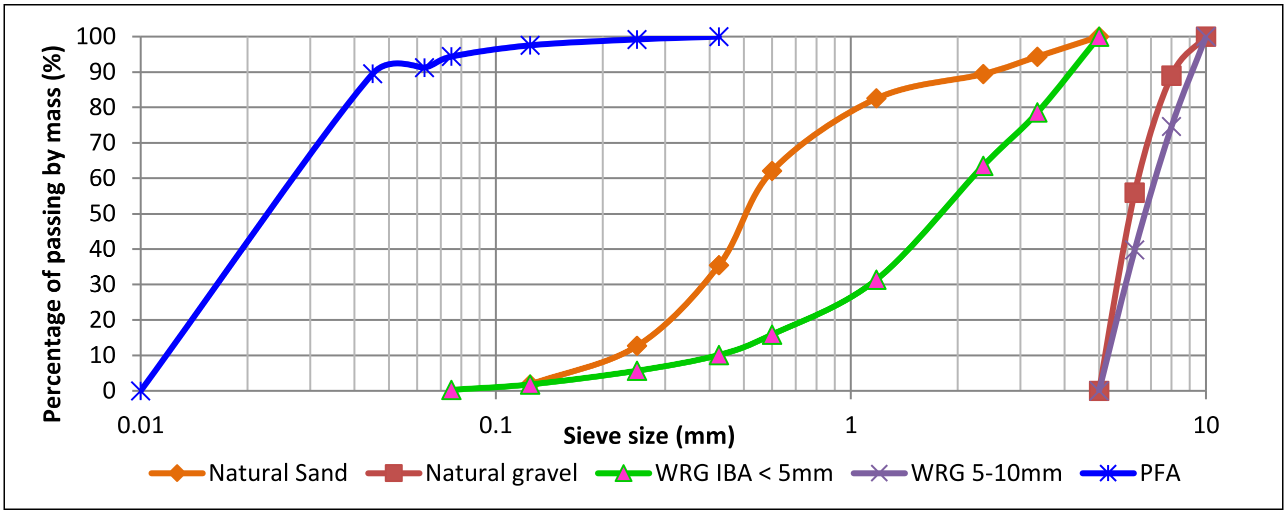


Figure 1. Gradation of the aggregates used in the investigation

Table 2. Typical properties of aggregates and filler used in the investigation

Properties	Gravel	Sand	IBA	PFA
Bulk density (g/cm^3)	1.58	1.51	1.16	0.63
Particle density (g/cm^3)	2.70	2.66	2.54	2.16
Moisture content (%)	0	0.5	25.6	11.27

2.1.4. Binders

The binder used in this investigation was a blended binder composed of glycerol and cooking oil with the mixing ratio of 3:1 by weight (Vu, 2012). Pure glycerol was ordered from the ReAgent Company, Cheshire, UK. The clean and waste cooking oil was collected from Leeds University Catering Service and which originally came from the KTC Company (Wednesbury, West Midland, UK). Waste glycerol was collected from the Greenegy Biodiesel production plant in Immingham, South Humberside, UK.

2.2. Testing and modelling methods

2.2.1. Compressive strength

Compressive strength of the sample was determined using a TONIPACT 3000 compaction machine. The testing procedure was in accordance with British Standard document BS EN 12390-3: 2002 (BSI, 2002). The size of the samples produced was 100 x 100 (base dimensions) x55mm high. The loading rate was selected at 3 MPa/s.

2.2.2. Water absorption and water stability

The water absorption test for all the samples in this investigation was in accordance with British Standard document BS EN 771 - 1: 2003 – Annex C (BSI, 2003). The method used was the 24 h cold water immersion test. Further investigation was also carried out to evaluate the water stability/reactivity of the binder by extending the immersion time period to 3, 5 and 7 days.

2.2.3. Initial rate of water absorption

The testing procedure for the initial rate of suction (IRWA) complied with the British Standard document BS EN 772-11:2000 (BSI, 2000a).

2.2.4. Mathematical Optimisation Modelling

There are many methods which can be used to build 'respond surfaces' (Box and Draper, 1987; Myers *et al.,* 2009); the commonly used Least Squares Method (LSM) was employed in this study. In order to utilise the response building method in the evaluation of this laboratory testing programme a strategy to develop the Design of Experiments (DoE) (Sacks *et al.,* 1989; Shewry and Wynn 1987; Johnson *et al.,* 1990; Jin *et al.,* 2003) was used, i.e. the Optimal Latin Hypercube (OLH) (Bates *et al.,* 2004; Toropov *et al.,* 2007; Audze and Eglais, 1977; Fuerle and Sienz, 2011).

The following example has two independent variables x and y and one dependent variable u in the second order relationship. For convenience, we define point z with the coordinate of x and y as shown in Figure 2. With the approximation function, $u(x,y) = u(z)$defined as a quadratic, the polynomial is as follows:

$$u(x,y) = u(z) = a_0 + a_1x + a_2y + a_3x^2 + a_4xy + a_5y^2 \tag{2.1}$$

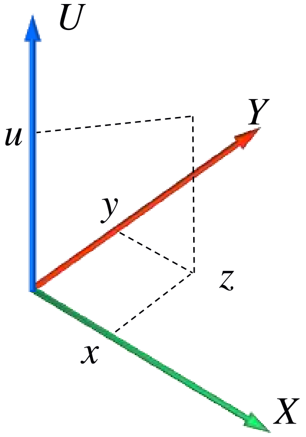


Figure 2. Two-parameter Least Squares Method illustration

For a given data set $(x_1, y_1, f_1), (x_2, y_2, f_2),\ldots, (x_N, y_N, f_N)$ where N ≥ 6, and the number of levels for x_i and $y_i \geq 3$ and assuming that $u(x, y)$ is the best fitting surface, the total square error has to satisfy the condition of a minimum:

$$E = \sum_{i=1}^{N} [f_i - u(x_i, y_i)]^2$$

$$= \sum_{i=1}^{N} [f_i - (a_0 + a_1x_i + a_2y_i + a_3x_i^2 + a_4x_iy_i + a_5y_i^2)]^2 = min \tag{2.2}$$

In this expression a_0, a_1, a_2, a_3, a_4 and a_5 are unknown coefficients whereas all the values of x_i, y_i and f_i are given. In order to satisfy the above condition, the unknown coefficients $a_0, a_1, a_2, a_3,$ $a_4$and a_5 must yield zero first derivatives of E. That means:

$$\frac{\partial E}{\partial a_i} = 0 \tag{2.3}$$

Solving Equation 2.3 will result in the value of the unknown coefficients $a_0, a_1, a_2, a_3, a_4$and a_5.

3. SAMPLE PRODUCTION

Samples were cold mixed; the dried raw materials were proportioned by weight. The total weight of the aggregate and filler acted as the base weight and the amount of binder used was calculated as a percentage of this base weight. Total binder content used ranged from 14 to 20% in which the mixing ratio of clean cooking oil and pure glycerol was 1:3.

When mixing was completed, the material was weighed and divided into 2 or 3 portions and placed into a mould in two or three stages. The material was manually compacted to ensure that the sample's corners were filled properly. The sample cross-section was 100 x 100 mm; a total amount of material of 1.0 – 1.3 kg was used depending on the required thickness/depth of the sample, which was between 50 to 70 mm. The samples were compacted using a 500 kN capacity press machine with compaction levels of either 1, 2, 4, 8, 16, 20, 24, and 32 MPa. A convection oven was used to cure the samples at temperatures of 140, 160, 180 or 200 ºC. Also, different curing durations were selected, namely 24, 48, 72, 96 and 120 h. Figure 3 shows a block sample after manufacturing; traditional brick geometries were also manufactured.

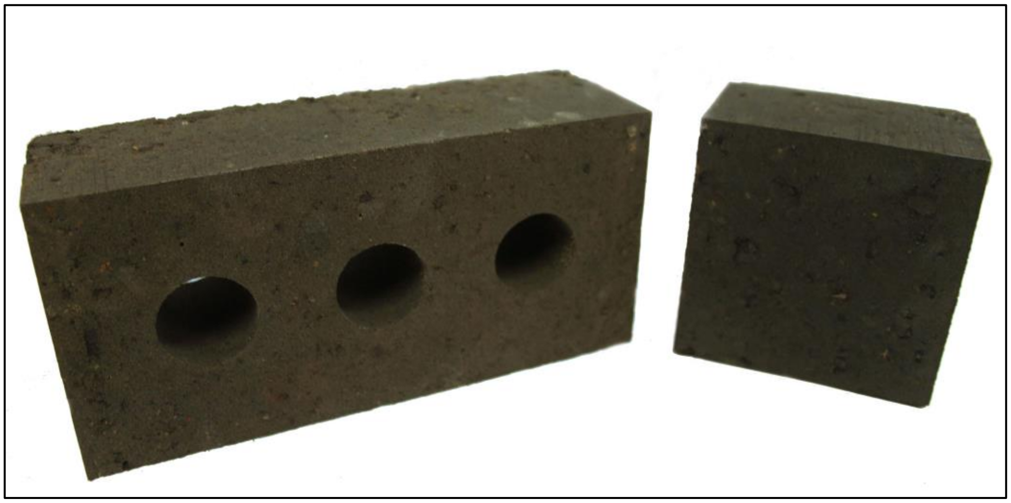


Figure 3. Brick and block samples

A laboratory optimisation was performed to identify the mix design and hence sample with the highest compressive strength. Three mix types were subsequently considered, namely: control samples (Mix A), pure blended binder samples (Mix B) and waste blended binder samples (Mix C). The samples were made using the parameters determined from the laboratory optimisation (i.e. 8 MPa compaction pressure, 160 ºC curing temperature and 96 h curing to time) to evaluate the performance of the final products. The compositions of these samples are as shown in Table 3below:

Table 3. Material composition of different types of samples

Materials	Type of sample Mix A (Control samples)	 Mix B** (pure binders)	 Mix C** (waste binders)
Natural gravel	30%		
Natural sand	70%		

IBA 5-10mm		30%	30%
IBA <5mm		70%	70%
PFA*	40%	40%	40%
Clean cooking oil	3.3%	4.5%	
Pure glycerol	10%	13.5%	
Waste cooking oil			4.5%
Waste glycerol			13.5%

Note: These are not absolute values, i.e.

**: percentage of filler is 40% by weight of total aggregate and filler*

***: percentage of binder calculated based on the total weight of aggregate and filler*

4. TESTING RESULTS AND DISCUSSION

4.1. Surface of the samples

Due to the nature of the raw materials, the fresh uncured samples had low strength and required careful handling. However, after being cured, they became solid and possessed higher strengths (see Figure 4 below). The final products also had smooth and flat surfaces with sharp arises.

4.2. Bulk density

The water replacement method was used to measure the bulk density of the samples. It was found that compaction pressure was a key factor influencing the bulk density of the samples. The bulk densities obtained for the cured waste and pure binder (Mix B and C) samples ranged from 1.64 to 1.83 g/cm^3. Control sample (Mix A) has the highest density of 1.91 g/cm^3. This was thought to be due to the higher porosity of the IBA aggregate which generated the lower density of Mix B and C hence better manual handling properties (and ultimately more economical transportation of product).

4.3 Compressive strength

Figure 4(a) showed that, with a curing temperature of 160 ^{o}C, the compressive strength of the samples increased when curing time increased from 24 to 72 or 96 hours, reaching a strength plateau of approximately 24 to 32 MPa depending on the binder content. The maximum compressive strength achieved was 32.22 MPa with samples containing 18% total binder content and which were cured for 96hours. This was also the maximum value of the entire testing programme. The lowest compressive strength obtained was 6.05 MPa; this was for a sample containing 20% total binder content and which was cured for 24 hours.

One of the key factors that influenced the compressive strength development was curing temperature. Figure 4(b) showed that for curing times up to 72 h, the compressive strength of the samples increased when the curing temperature increased from 140 to 180 ^{o}C. The strength then decreased when the curing temperature increased to 200^{o}C. For curing times above 72 h, the strength increased only when curing temperature increased from 140 to 160 ^{o}C and it decreased when the curing temperature exceeded 160 ^{o}C. It could be concluded that the best curing temperature would be in the range of 160 to 180 ^{o}C.

It is believed that the level of binder oxidation directly involves in strength development of samples. Longer curing time leads to more binder oxidation resulting in higher compressive strength. Similarity, higher curing temperature leads to quicker oxidation process of binder. Therefore, higher curing temperature resulted in faster strength development. However, if the temperature was too high (over 200 °C) the binder might be broken down due to the high heat acting for a long time (more than 18 hours) (Vu, 2014).

Figure 4(c) illustrated the influence of binder content on the compressive strength of the samples. For curing times more than 24 h, the strength of the samples increased when the total binder content increased from 14 to 16 or 18%. Beyond 18%, the strength decreased. In the case of curing time for 24 hours, it was thought that the curing duration was insufficient to fully cure the samples. Therefore, the more binder the lower strength sample.

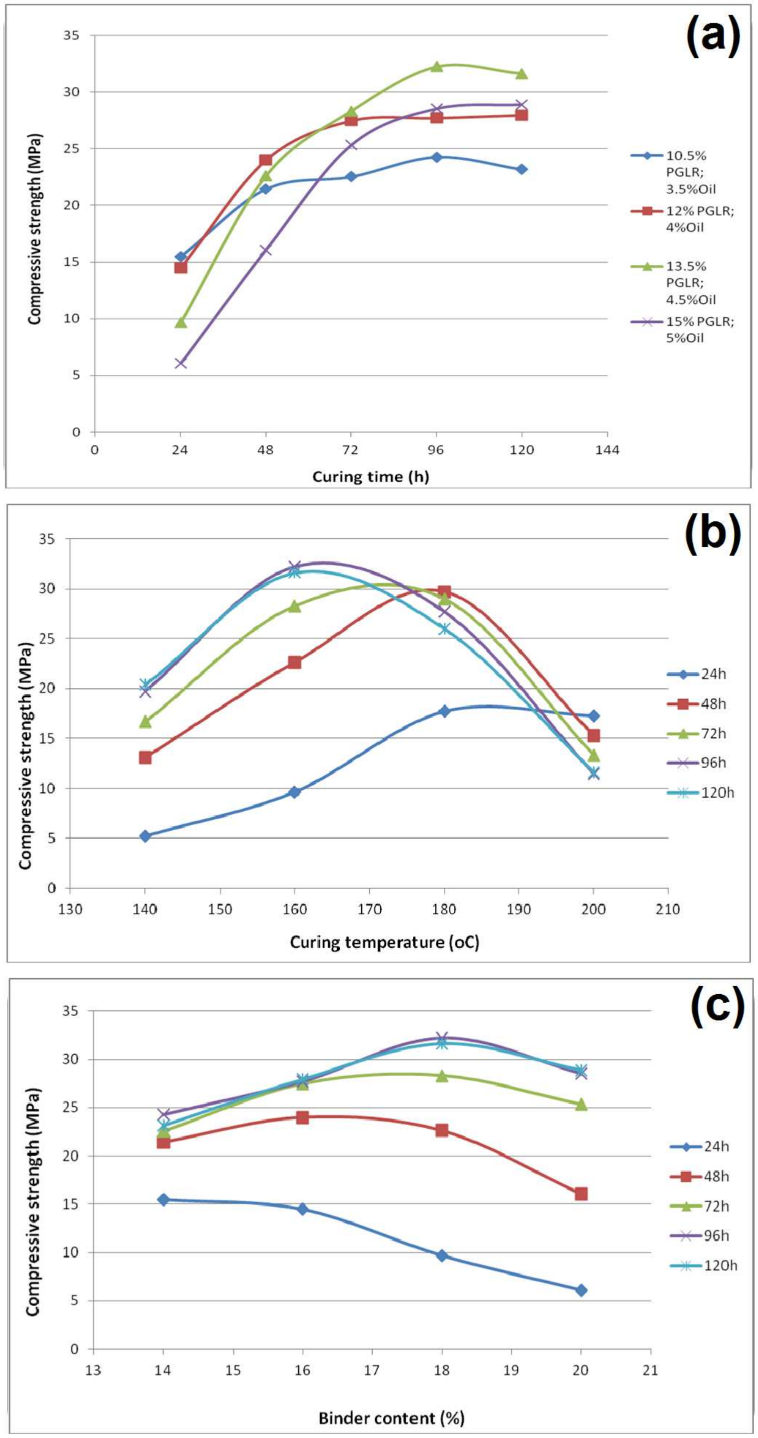


Figure 4. Compressive strength (MPa) vs. (a) Curing time (h) at 160 °C curing temperature (b) Curing temperature (°C) for samples with 18% total binder content (c) Binder content (%) at 160°C curing temperature

(Note: (a) These observations reflect the frequency of the data points and are therefore at worst within 10 °C, however, based on previous research using bitumen and vegetable oil binders these observations are in line with those investigations).

According to the laboratory optimisation study, the samples produced with 18% total binder content and cured at 160 °C for 96 hours had the highest compressive strength of 32.2 MPa. These values were used to produce samples with waste binders (Mix C) which were then compared with the control samples made from natural aggregates (Mix A) and pure binders (Mix B).

Table 4 showed a comparison of some of the key properties of the control sample with pure binder and waste binder samples. The figure showed that the compressive strength of the pure binder samples (Mix B) was 12.5% weaker than that of the control samples (Mix A). This could possibly be explained by the high porosity of the IBA particles (Vu and Forth, 2014) which helped produce samples with a lower strength in comparison with those containing natural gravel particles. The use of IBA also lead to higher binder requirements, i.e. 18% compared to 13.3% for the control samples. The higher water absorption properties for Mix B and C also indicated that the porosity of the IBA was still active and had not been negated by the higher binder content.

Table 4. Compressive strength of control sample, pure binder and waste binder samples

Properties	Natural aggregates (Mix A)	Pure binders (Mix B)	Waste binders (Mix C)	Recommended value
Compressive strength (MPa)	38.4	33.6	31.3	≥ 5 for Damp proof course 1,2 (BS 3921: 1985)
Water absorption (%)	7.26	8.03	8.15	No limits for other types of bricks (BS 5628 part. 3: 1985)
Initial rate of water absorption (kg/m2.min)	0.067	0.117	0.083	≤ 1.5 (BS EN 772-11:2000)

Table 4 also showed that the compressive strength of the waste binder samples (Mix C) was about 93.1% of the pure binder samples (Mix B) and 81.5% of the control sample (Mix A). It should be noted that the strength of these samples was reasonably high and still much higher than the required compressive strength of current commercial concrete blocks used in the UK (Uwe, 2012). Mix B and Mix C used the same amount of aggregates and binder whereas the waste glycerol used for Mix C only contained up to 92% glycerol (Vu, 2012). Therefore, the drop in compressive strength of Mix C in comparison with Mix B was reasonable as there was an effective decrease in active binder content; impurities constitute the remaining 8% of the waste glycerol.

4.4. Water absorption and water stability

Figure 5(a) demonstrated the change in water absorption with time of the different samples. For all types of samples, the water absorption increased gradually when the soaking time increased from 1 to 7 days. The control sample had a lower water absorption than the pure binder (Mix B) and the waste binder (Mix C) samples. In general, the water absorption of all samples was between 8.1 to 9.2%. It is predicted that the water absorption of the samples will continue to increase after 7 days of soaking. This could be explained by the presence of glycerol as part of the blended binder. Initially, it was believed that the glycerol forms a thin coating on the outer surfaces of the aggregate and filler particles as well as on the surface of the exterior pores. The presence of this thin film would firstly protect the particles from the penetration of water because it creates a physical barrier to absorption and because the hydrophilic glycerol ‘attracts’ water by nature it inhibited the flow of water through the matrix. These points might clarify the reason for the longer time taken to make the sample fully saturated, i.e. compressive strength test of samples showed that after three days soaking in water (without drying), a ’dry core’ could still be observed inside the failed sample after crushing. This confirmed that the sample had not been fully soaked.

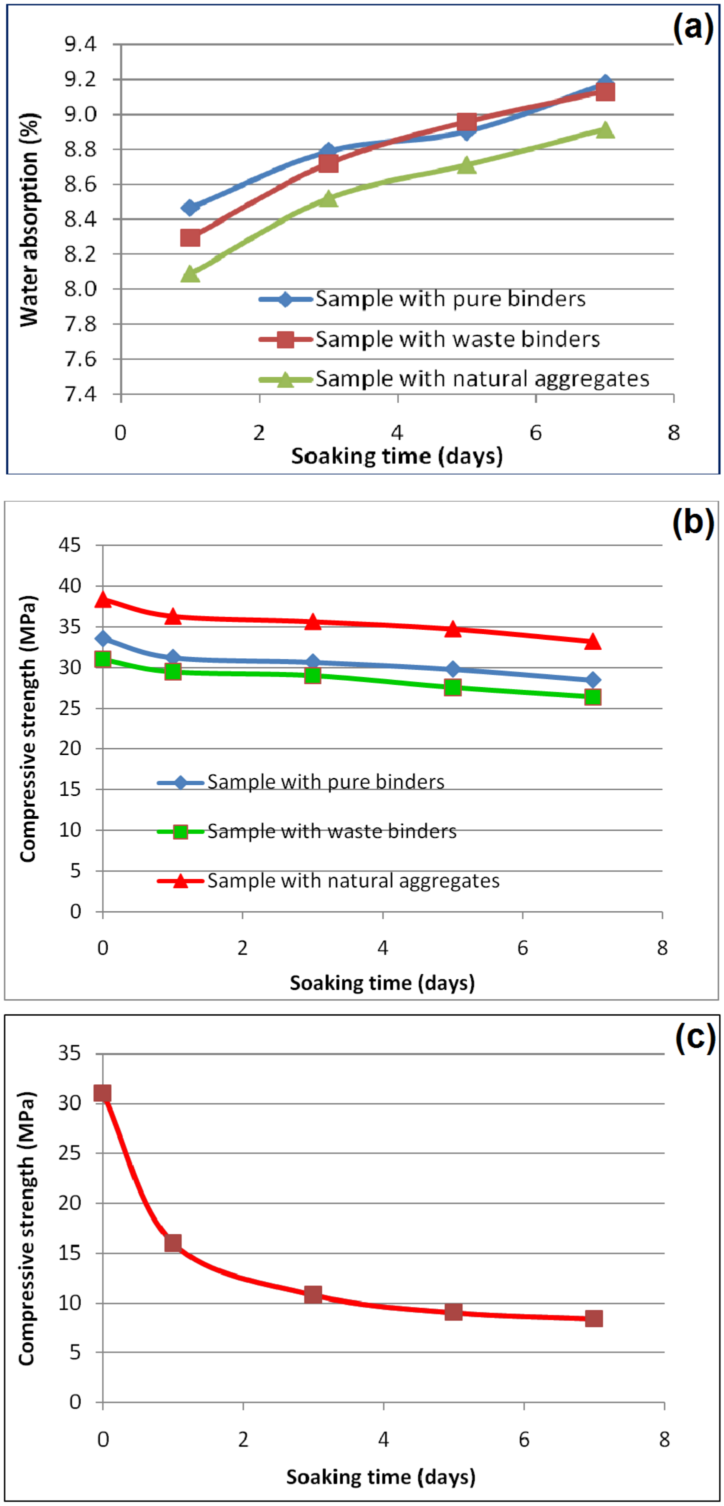


Figure 5. (a) Water absorption (%) vs. Soaking time (days)for different samples (b) Compressive strength (MPa) vs. Soaking time (days) for different samples (c) Saturated compressive strength of waste binder sample (MPa) with different soaking time (days)

Figure 5(b) illustrates the decrease in compressive strength of samples in relation to soaking time periods. After being soaked, the samples were dried at 105 ºC for 48 hours to recover the 'dried state'. The compressive strengths of the control samples (Mix A) after 1 and 7 days immersion were 36.33 and 33.23 MPa, respectively; these strengths were 5.4 and 13.5% weaker than the original strength (38.4 MPa). Similarly, the decrease in strength of Mix B and Mix C after 1 and 7 days soaking were 6.9 and 16.1% and 5.8 and 15.7%, respectively. However, after 7 days soaking, the strengths of all of the samples were still greater than 80% of the original strength. The percentage reduction in strength after soaking was surprising (it was expected to be higher – see below). However, it was thought that the drying process restored some of the bonding within the matrix.

An additional study was therefore carried out to investigate the decrease in saturated compressive strength (without drying) of samples under different immersion times. Figure 5(c) shows the changes in saturated strength of the Mix C samples after soaking from 1 to 7 days. It can be seen that during this time, the strength decreased to 16 MPa and 8.1 MPa, respectively. These strengths were between 50 and 25% of the original strength of Mix C sample. These losses in strength were more in-line with what was expected. Traditional clay bricks and concrete blocks exhibit even lower saturated strengths due to the modulus of the water in the pores and the internal negative pressure systems this creates within the units (when unsaturated, the pores are filled with air of effectively zero modulus) (Henry *et al.,* 2004).

The loss of strength observed in the mixes of this investigation can also perhaps be explained by the neutralising effect of the water and the partial dissolution of the hydrophilic glycerol during immersion which subsequently leaches out into the water. It is thought that the penetration of water into the samples neutralises the polarised bonding of the cured glycerol with the aggregates by adding the H^+ and OH^- ions from the water to the polarised glycerol molecule (see Figure 6) (Vu and Forth 2014). The partial glycerol loss (leaching) from inside the unit may also explain the slow and prolonged raise in water absorption mentioned above, as the aggregates become exposed (with the removal of the glycerol) and consequently saturated through the immersion process. Despite the loss in strength, after 7 days soaking, the saturated strength of the waste binder samples was still greater than those of concrete blocks currently used in the UK (Uwe, 2012). Generally, these tests indicated that the samples were robust even when saturated.

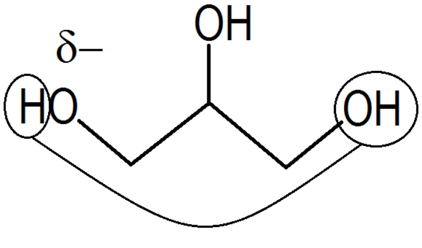


Figure 6. The dehydration of a glycerol molecule

4.5 Initial rate of water absorption

It can be seen from Table 4 that the mean IRWA of Mix A, Mix B and Mix C samples were between 0.067 to 0.117 kg/m^2.min. These values are well below the maximum IRWA recommended in BS5628 Part 3 (BSI, 1985b) which is 1.50 kg/m^2.min but still sufficient to promote good bond with the mortar. Results also showed that the IRWA of the pure binder and waste binder samples were higher than that of control samples. This was thought to be due to the higher porosity of the IBA aggregate enhancing the intake of water. A study carried out by Dong (2006) showed that the IRWA of samples using bitumen as a binder and incorporating different types of aggregates and filler was less than 0.05 kg/m2.min. Also, the water absorption of these samples was less than 6%. These values were smaller than those from this investigation in which hydrophilic glycerol was used as one of the binder constituents. Hence, it is believed that the dehydrated glycerol (Vu and Forth 2014) was also the cause for the higher IRWA and water absorption in these samples.

5. OPTIMISATION PROBLEM

This section attempts to create an empirical model of compressive strength as a function of the three input parameters. The output from the subsequent numerical optimisation is then compared with the values obtained from the experimental investigation. Initially, a conventional experimental optimisation was carried out to identify the best compressive strength of the samples in terms of curing time, curing temperature and binder content. However, such experimentation requires a large number of samples to be manufactured and this is an issue in terms of efficiency. According to the initial experimental trial test results carried out by Vu (Vu, 2012), compressive strength of the sample is mostly influenced by:

- Binder content: 14, 16, 18, 20% (4 levels) – which will be known as x_1
- Curing temperature: 140,160,180, 200 °C (4 levels) – which will be known as x_2
- Curing time: 24, 48, 72, 96, 120 h (5 levels) – which will be known as x_3

As mentioned previously, the compressive strength was selected as the primary indicator of the material quality. Hence the optimisation problem can be formulated as follows:

Find the combination of parameters x_1 (binder content),x_2 (curing temperature) andx_3 (curing time)that maximises compressive strength as a function $F(x_1,x_2, x_3)$, where $x_1$varies between 14 and 20%, x_2 varies between 140 and 200 °C and x_3 varies between 24 and 120 h.

Initially, all tested combinations of x_1,x_2 and x_3 can be considered as a 'Design of Experiments (DoE)' and each combination can be represented as a point in a3-dimensonal spacex_1, x_2 and x_3. All the experimental results were used to generate an empirical model representing a full DOE of 80 points (3 tests per point; 240 experiments in total) as shown in Figure 7(a).

The aim was then to evaluate the validity of the subsequent empirical models built by selecting a smaller number of the experimental sample results. This was achieved by investigating the dependence of the predictive quality of the empirical models built by LSM regression (Box and Draper, 1987; Myers *et al.,* 2009) on the different amount of experimental data, i.e. the number of

DoE points. A Permutation Genetic Algorithm (PermGA) (Bates *et al.,* 2004; Toropov *et al.,* 2007) was used to create a DoE with a certain number of points using the concept of an Optimal Latin Hypercube. A number of initial random DoEs were created. They were used as the first generation (parents) of the population. By using the crossover and mutation operators, a new generation (children) were created. Each child in the population was then assessed and selected as the parent for the next circle using the potential energy criteria (Bates *et al.,* 2004; Toropov *et al.,* 2007). If the child has a high value of potential energy, it will be eliminated. After a predetermined number of reproduction cycles, the child that has the lowest potential energy value will be the best solution (for the DoE). After a DoE was established for a given number of points, the three experimental results at each of the DoE points were used as the input data for the HyperStudy 11.0 (Altair Engineering, 2008) software to generate a polynomial response model.

Different numbers of samples (i.e. 1, 2 or 3) were used to create the response surfaces (Vu, 2012).

In this paper, only DoEs with 20, 40 and 60 points were generated. A genetic optimisation was then used to examine the parameter space to find the optimal combination of the variable x_1, x_2 and x_3 that generates the maximum compressive strength of the sample. Figure 7(b), (c) and (d) illustrate the Design of Experiments of the space x_1, x_2 and $x_3$with 60, 40 and 20 points, respectively. The normalised minimal point distance distributions of the systems are shown in the corresponding

Figure 8(a), (b) and (c). The point distance figures show the normalised minimum distances from the current point to all the rest of the points in the DoE. Therefore, no unit was used. It can clearly be seen that the distribution of points is very uniform as the variation in the minimal distance is relatively small. This exhibits a good distribution of points in the surveying space of the parameters x_1, x_2 and x_3.

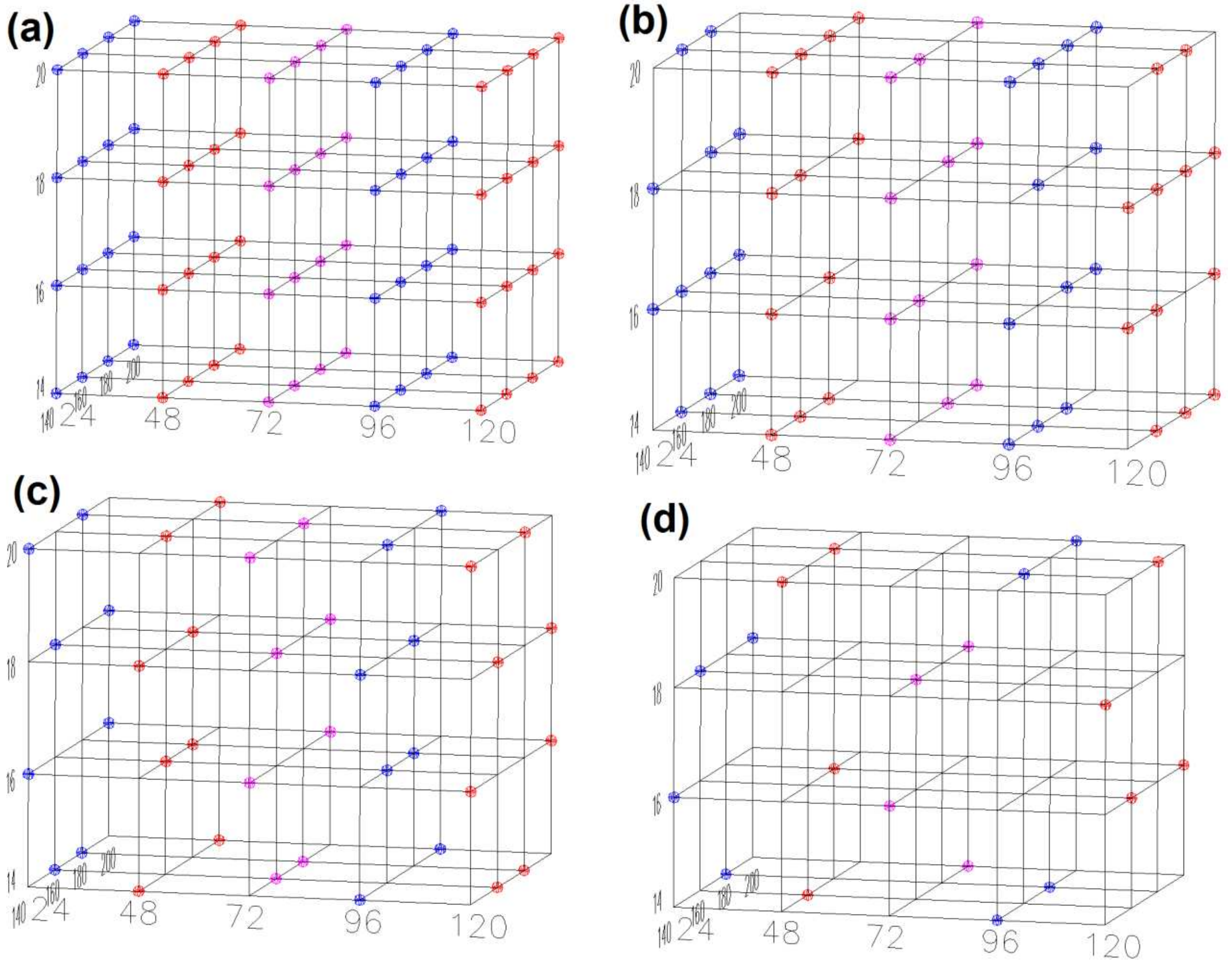


Figure 7. (a) Full Design of Experiments plot in the space of parameters x_1, x_2 and x_3 (b) DoE of 60 points (c) DoE of 40 points and (d) DoE of 20 points

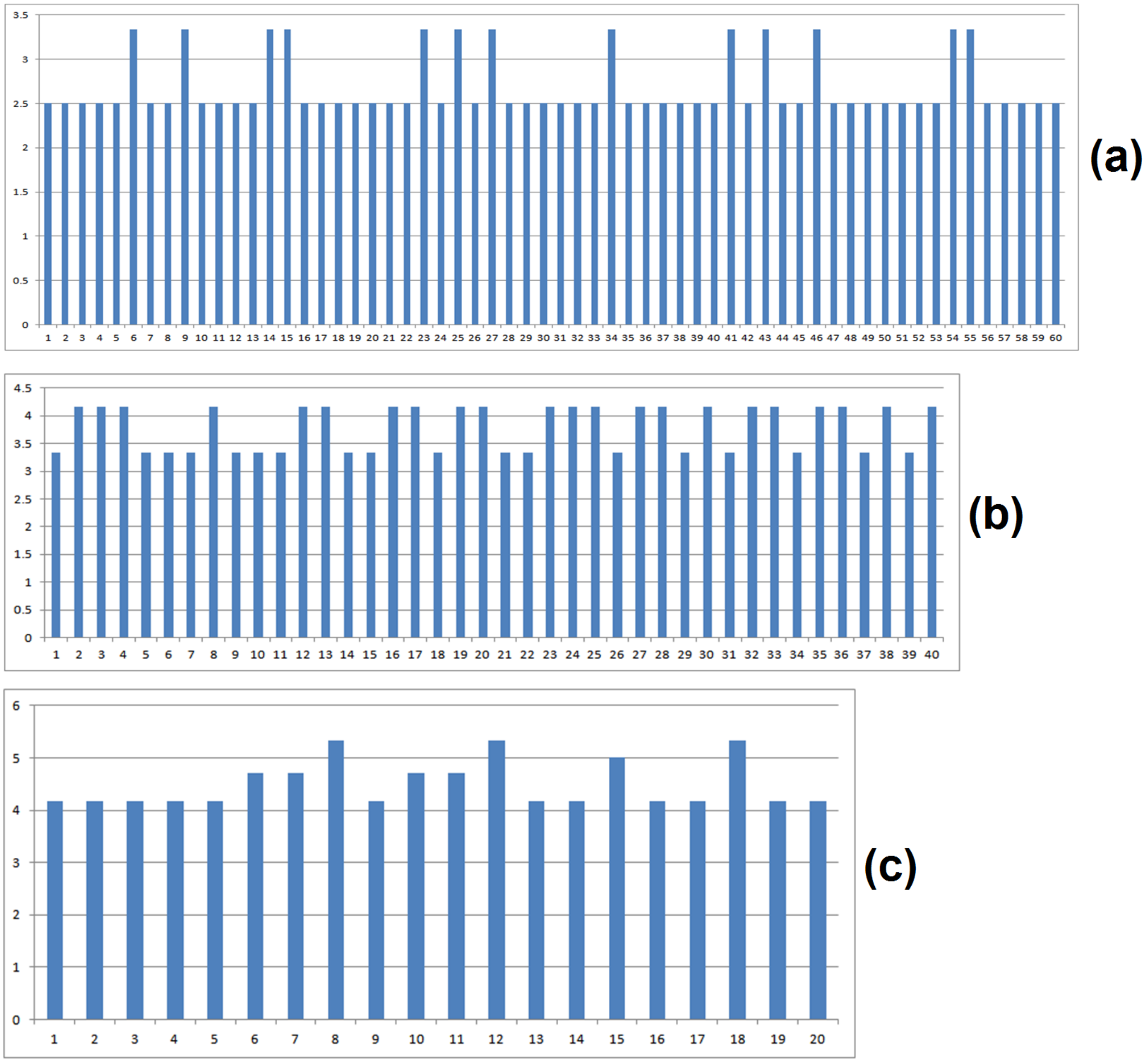


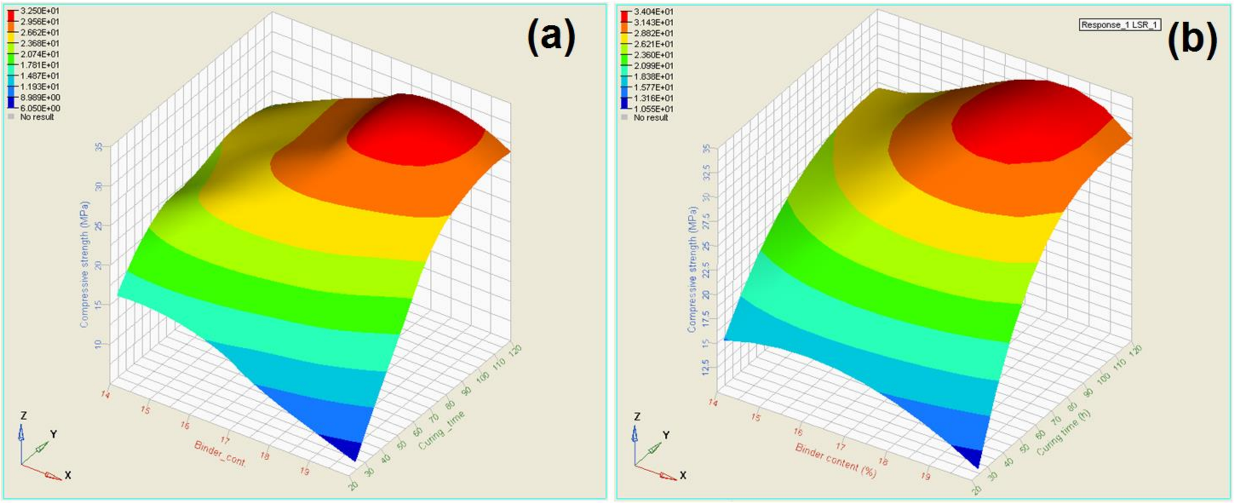
Figure 8. Point distance distribution in (a) 60 points DoE (b) 40 points DoE and (c) 20 points DoE

In order to build the response surface for the entire test plan (the full DoE), all the combinations of parametersx_1, x_2 and x_3 can be used as a DoE in which each point represents one combination as shown in **Error! Reference source not found.** The function for the response surface can be defined as $F(x_1, x_2, x_3)$ – a function representing the compressive strength, and the optimisation algorism will be used to search for a combination of x_1, x_2 and x_3 that maximises the compressive strength approximation function.

Using the results from 240 experiments as the database for the HyperStudy 11.0 software, an uncompleted fourth order polynomial approximation was selected to create an analytical model expression of the sample's compressive strength $F(x_1, x_2, x_3)$. The result was found as follows:

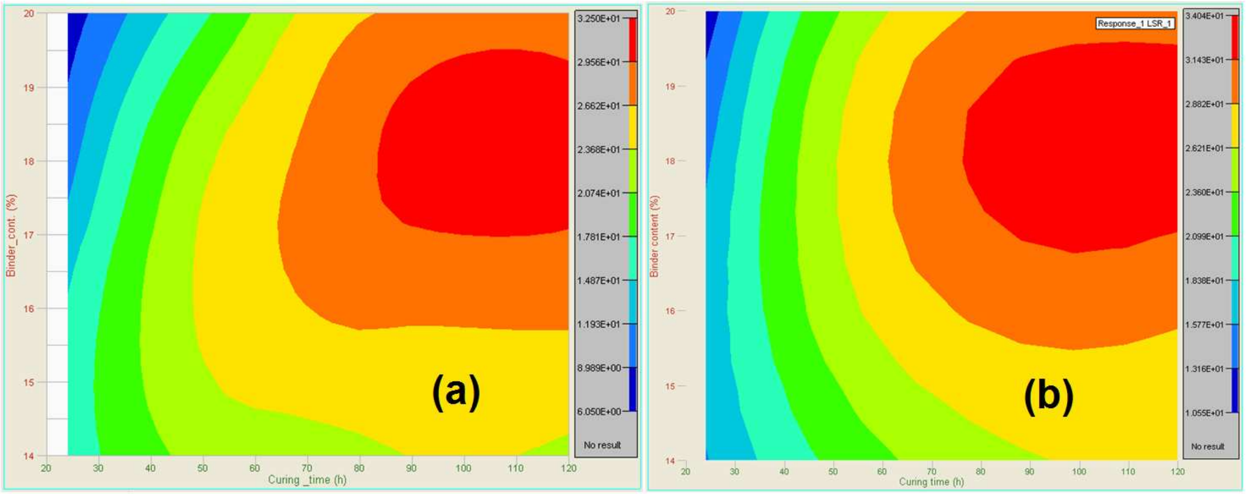
$$F(x_1, x_2, x_3) = 3374.1297 - 37.344147 x_1 - 62.100298 x_2 - 35.28512 x_3 - 7.0174167 x_1^2 + 0.3169613 x_2^2 + 0.1088791 x_3^2 + 2.1280213 x_1 x_2 - 1.1270852 x_1 x_3 + 0.6528087 x_2 x_3 + 0.3022118 x_1^3 - 4.39E\text{-}04 x_2^3 - 9.53E\text{-}05 x_3^3 - 0.0203948 x_1^2 x_2 - 0.0098791 x_1 x_2^2 + 0.0805577 x_1^2 x_3 - 0.002642 x_1 x_3^2 - 0.0034394 x_2^2 x_3 - 9.52E\text{-}04 x_2 x_3^2 + 0 x_1^4 + 0 x_2^4 + 0 x_3^4 - 0.001575 x_1^3 x_2 - 9.58E\text{-}07 x_1 x_2^3 - 0.0017325 x_1^3 x_3 + 2.80E\text{-}06 x_1 x_3^3 + 5.88E\text{-}06 x_2^3 x_3 + 3.91E\text{-}07 x_2 x_3^3 + 2.95E\text{-}04 x_1^2 x_2^2 + 5.11E\text{-}05 x_1^2 x_3^2 + 2.63E\text{-}06 x_2^2 x_3^2 \quad \textbf{(5.1)}$$

The response surface was then built based on the approximation function above and visualised as the contour plot at the curing temperature of 160°Cwhich generated the highest compressive strength sample in laboratory investigation. This surface plot is also compared with the surface built from input data at the same curing temperature. Figure 9 and Figure 10show the 3-D and contour plot of these surfaces.



(a) (b)

Figure 9. 3-D view of surface built from (a) raw data and (b) model of 240 samples at 160°C



(a) (b)

Figure 10. Contour plot of surface built from (a) raw data and (b) model of 240 samples at 160°C

Figure 9 and Figure 10 show little difference between the surface built from the 240 experimental results using the Least Squares Method and the surface built from the input (modelled) data at 160°C curing temperature. The curvature of the contours from the model developed using the 240 samples (b) is more uniform than those from the input data surface (a). This can be explained by the fact that the Least Squares Method tends to yield a harmonised result (response surface) to fit all the input data. In Figure 10(b), the red dot area shows the optimum region for the desired compressive strength and the mathematical optimum value is located at the middle of this region. It also shows that the boundary of this optimal region is from about 16.8 to 19.6% in binder content and 78 to 120 hours in curing time. This area is slightly bigger than the area obtained from input data.

The approximation function (Equation 5.1) was then maximised with respect to the x_1, x_2 and x_3 results in the following parameters' values: total binder content $x_1 = 18.36\%$; curing temperature 164.8 °C and curing time $x_3 = 96.6$ h returning a value of $F(x_1, x_2, x_3) = 34.39$ MPa in compressive strength. To directly assess the accuracy of this model, a comparison can be made with the average conventional experimental optimisation result of 32.22 MPa at $x_1 = 18.00\%$; $x_2 = 160$ °C and $x_3 =$ 96 h. The model's response at the same co-ordinates (at $x_1 = 18.00\%$; $x_2 = 160$ °C and $x_3 = 96$ h) can be assessed and this returned 33.88 MPa as the estimated strength. This produces an error of only 5%.

Using the same procedure, DoEs of 20, 30, 40, 50, 60 and 80 points with different experimental numbers (1, 2 or 3) of samples at each surveying point were evaluated. For models built form 40, 50, 60 and 80 points, the data set is sufficient to build the uncompleted fourth order models, and the number of coefficients is 28 (a_0 to a_{18} and a_{22} to a_{30}). For models built form 20 and 30 points, the data set is only sufficient to build the uncompleted third order models, and the number of coefficients is 15 (a_0 to a_9 and a_{13} to a_{18}) (Vu, 2012) . The error between the experimental and model values are also calculated for each model at the point with the coordinate of $x_1 = 18.00$ %;

x_2 = 160 °C and x_3 = 96 h. The model error is determined as the difference between the model response value (checking value) at the predetermined coordinate and the real test result at the same point.

Table 5. Maximum value of models using Least Squares Method

Model	Number of samples	Variable			Max value (MPa)	Error* (%)	R^2
		x1	x2	x3			
LSM 80 points (3 samples/point)	240	18.36	164.80	96.60	34.39	6.75	0.9501895
LSM 80 points (2 samples/point)	160	18.10	159.91	114.18	30.93	4.01	0.9490799
LSM 80 points (1 sample/point)	80	18.15	158.96	113.07	28.32	12.10	09504982
LSM 60 points (3 samples/point)	180	18.21	158.62	120.00	29.29	9.09	0.9587833
LSM 60 points (2 samples/point)	120	18.20	159.58	105.10	29.05	9.84	0.9593692
LSM 60 points (1 sample/point)	60	18.22	159.89	96.95	27.52	14.59	0.9574717
LSM 50 points (3 samples/point)	150	17.75	166.88	85.61	30.91	4.07	0.9562113
LSM 50 points (2 samples/point)	100	17.47	163.30	93.81	28.27	12.25	0.9562732
LSM 50 points (1 sample/point)	50	18.05	166.13	86.91	33.34	3.47	0.9582848
LSM 40 points (3 samples/point)	120	18.30	168.25	91.73	39.61	22.93	0.9541079
LSM 40 points (2 samples/point)	80	17.86	164.68	87.27	28.04	12.98	0.9534284
LSM 40 points (1 sample/point)	40	18.03	163.41	89.47	28.35	12.02	0.9546788
LSM 30 points (3 samples/point)	90	18.03	164.48	105.21	29.95	7.05	0.9252225
LSM 30 points (2 samples/point)	60	17.90	164.02	105.48	29.42	8.70	0.9258641
LSM 30 points (1 sample/point)	30	17.84	164.53	109.72	29.91	7.17	0.9333729
LSM 20 points (3 samples/point)	60	18.20	166.11	99.20	30.86	4.23	0.9457337
LSM 20 points (2 samples/point)	40	18.19	166.18	98.99	30.64	4.92	0.9507922
LSM 20 points (1 sample/point)	20	17.77	165.35	104.34	30.41	5.61	0.9568139
Average		18.03	163.62	100.20	30.51	5.30	

** The error (%) is calculated as the differential the model's maximum value with the laboratory optimisation value of 32.22 MPa at* x_1 = 18%, x_2 = 160 ºC, x_3 = 96 h

The results show that the checking value and the model error vary and show no consistent trend with regards to the number of DoE points or number of sample per DoE points. Therefore, it can be concluded that there is no clear relationship between checking value or model error and the number of DoE points or number of sample per DoE point. This means that it is not always true to assume that a reduction of the model error (improving the accuracy) can be achieved by increasing the number of points or samples' results used within the model. In addition, the maximum value of the strength response for different models is also calculated together with the optimum value of the parameters in each model x_1, x_2, x_3 are also shown in Table 5.

Table 5 also shows that the maximum values predicted by the models built from the Least Squares Method with the number of points from 20 to 80 varies from 27.52 to 34.39 MPa, while the average value is 30.51 MPa. The standard deviation of this range of values is 0.66. It can also be seen that the range of the optimum value of the parameters are: x_1: from 17.47 to 18.36%; x_2: from158.62 to 166.88 ºC; x_3: from 85.61 to 120 h. These values are well within the optimal region defined in Figure 10(b).

In agreement with the checking value and model error above, it can also be seen in Table 5 that the maximum predicted value by the models built from different number of samples' results varies without a clear trend with respect to the number of DoE points, number of sample per DoE points and fitness coefficient R^2.

The results show that model built from a 20 point DoE with only 1 sample per point (20 samples used) has a model error of 7.69%. While the model built from the full 80 point DoE with 3 sample's results per point (240 samples used) still has a model error of 5.15%. Moreover, the optimum value of the model parameters: x_1= 17.77%, x_2= 165.35 ºC, x_3= 104.34 h are also well within the optimum region defined in Figure 10(b). Therefore, it can be concluded that a model built from only 8.33 percent (20/240) of the total experimental samples can still potentially predict the optimum value of the laboratory experiment results.

6. CONCLUSION

Samples using a blend of glycerol and cooking oil could be produced with a level of performance that is at least comparable to those of current traditional UK masonry units. The product appeared to have a fairly high compressive strength (more than 30 MPa) and even the saturated compressive strength is 8.1 MPa, which was higher than that of normal concrete blocks. It is recommended that, even exposed to saturated conditions, the strength of these units is still favourable. However, leaching of glycerol may be an issue and needs further investigation.

In terms of sustainability, the products developed in this study are promising; they will allow the utilisation of a large amount of waste materials such as incinerator bottom ash, pulverised fuel ash, waste glycerol and waste cooking oil. Furthermore, the recommended curing temperature was only 160ºC (much lower than traditional clay bricks), which helps to reduce the energy required for manufacturing. Shorter curing durations should also be possible in the future either to produce lower grade products suitable for different purposes or identified during the scaling-up process (to full manufacture scale), resulting in even lower energy requirements.

Waste glycerol and cooking oil could be used to produce samples with compressive strengths of 93% of those using pure binder. However, the glycerol content found in the crude glycerol was only actually 92%. A comparison of the other properties of the two sample types (waste and pure binder) indicated that they were relatively similar in performance. It therefore appeared that the use of waste binder was very efficient and that the impurities in waste cooking oil and waste glycerol were insignificant with respect to the sample performance.

An experimental investigation could be significantly enhanced using the empirical modelling and optimisation techniques. For the 3-parameter problem, using the LSM modelling method could reduce the number of laboratory experiments by up to 90%.

Although the modelling technique was applied for a new type of material (glycerol bound) and three parameters had been considered, the results showed that the model is still capable of predicting the optimum results of the laboratory testing programme. This confirmed the validity of the model for use in construction material development. By considering one more parameter in a 3-parameter problem, the modelling technique had produced a further 40% reduction in the number of experimental samples required as compared with a 2-parameter problem.

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