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PII: S0959-6526(15)01245-7

DOI: 10.1016/j.jclepro.2015.09.024

Reference: JCLP 6112

To appear in: Journal of Cleaner Production

Received Date: 7 April 2015

Revised Date: 29 July 2015

Accepted Date: 8 September 2015

Please cite this article as: Molineux CJ, Newport DJ, Ayati B, Wang C, Connop SP, Green JE, Bauxite residue (Red mud) as a pulverised fuel ash substitute in the manufacture of lightweight aggregate, *Journal of Cleaner Production* (2015), doi: 10.1016/j.jclepro.2015.09.024.

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# Bauxite residue (Red mud) as a pulverised fuel ash substitute in the manufacture of lightweight aggregate

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#### ABSTRACT

This study looked at the potential of bauxite residue or red mud to be used in the manufacture of lightweight aggregate in replacement of pulverised fuel ash (PFA), commonly used as a way of recycling problematic wastes. The percentage replacements of red mud with PFA were as follows: 25, 31, 38, 44 and 50%. These were blended in a mix with waste excavated clay and sewage sludge – all from the Chongqing municipality in China. Lightweight pellets were produced using a Trefoil rotary kiln and were sintered to 1200 °C. Results showed that 44 % bauxite residue replacement produced lightweight pellets with the highest compressive strength, highest density and largest water holding capacity. This would be expected in materials with a low level of silicates, which causes insufficient glass phase viscosity and therefore poor bloating during firing; producing an aggregate with a higher density but with open pores that allowed for larger water absorption. All ratios of red mud aggregates were significantly reduced in pH after firing to around pH 8, and this reduced the leachability of the aggregates to levels below those set by the European landfill directive (2003/33/EC)..

Key Words: Red mud, Recycled aggregate, Secondary product, PFA, Trefoil rotary kiln

#### 1. Introduction

Waste by-products are produced as a result of most industrial processes. Many of these materials are difficult to dispose of due to their hazardous nature, i.e. heavy metal content, leaching of environmental contaminants or fine particle size causing air pollution. Thus, a sustainable solution of recycling materials into secondary products, which are also of value, is desirable. Examples of notable by-product materials are: pulverised fuel ash (PFA), municipal solid waste incineration ash (MSWIA), sewage sludge, river silt and bauxite residue. Pelletising and firing these material is one innovative way of utilising them in order to produce a manufactured aggregate that can replace those made from natural resources. This is a principle that has been well established in recent years by researchers such as: Wainwright and Cresswell, 2001; Aineto et al. 2005; Sarabèr et al. 2012; Cheeseman and Virdi, 2005; Cheeseman et al., 2005; Pioro and Pioro, 2004; Van der Sloot et al., 2001 and Tang et al., 2011. This technology also provides environmental benefits; as many of these by-products contain heavy metal contaminants, which become encapsulated in a silicate matrix structure when sintered at high temperature, making them non-volatile vitrified residues with low leachability (Chang et al., 2007).

Aggregates are generally formed with two types of waste; a bulking material and a fuel material. Bulking materials make up the structure of the aggregate, such as PFA (Ahmaruzzaman, 2010), MSWIA (Hwang et al. 2012), ash from combined heat and power combustion of paper sludge (Liaw et al. 1998), shale and clays (Laursen et al. 2006) and aggregate crushing fines and glass fines (Kourti and Cheeseman, 2010); whilst the fuel material can be any biodegradable material with high calorific value in dry or slurry form, such as sewage sludge (Fytili and Zabaniotou; 2008), biodegradable municipal waste or farming slurry. They are mixed together and pelletised, forming 'green pellets', before being dried and fired up to 1200 °C. The density of lightweight aggregates is associated to expansion (bloating) of raw materials. For materials to expand, firstly, they must produce a viscous glass phase at high temperature to encapsulate a gas and secondly, contain a substance that will liberate a gas at that temperature (Riley, 1951). Presence of particular oxides in unfired materials controls the viscosity of the glass phase, and it is the viscosity that controls the pore structure by entrapping the liberated gas. Therefore, it can be inferred that presence of viscosityregulating oxides directly affects the pore structure (i.e. size, shape, distribution etc.) and thus, have an effect on a number of inter-relating properties such as: density, water absorption and compressive strength. (Lin, 2006, González-Corrochano et al., 2011). Depending on water absorption capacity, the manufactured aggregate can be used in a range of applications, from concrete production to use as a component of growing media for green roofs (Molineux et al. 2009; Molineux et al. 214) and other forms of urban greening (Francis and Lorimer 2010). A low water absorption capacity would be required for use in lightweight concretes to ensure a sufficient curing process is achieved, however a high water absorption capacity would be highly desirable in growing media where plants would have more access to water. Therefore, in order to evaluate the performance of aggregates for various secondary applications, the main parameters controlling water absorption and density (i.e. pore structure of aggregates) must be investigated (Swamy and Lambert, 1981).

In this study we aimed to produce lightweight aggregate from a mixture of bulking materials; waste clay (from excavations), PFA, bauxite residue (also known as red mud) and a fuel material; sewage sludge. The PFA captured from the stacks of coal fired power stations, has been used for many years in aggregate production (Anon, 1963; Terukina et al. 1993; Owens 1993) but has also been used in concrete production, soil stabilisation and as a fertiliser. Originally seen as a waste product that was sent to landfill, its pozzolanic properties have led to it being considered as a commodity rather than a waste product (Owens 1993). In the Netherlands, for example, two plants producing light weight aggregate were closed due to more and more PFA being used as pozzolanic filler in concrete (Sarabèr et al. 2012). Therefore it would be advantageous to find another waste that could be utilised in aggregate production as PFA is becoming less available. Bauxite residue or red mud is a by-product in the manufacture of alumina (Gräfe et al. 2009) and its composition varies depending on geographic origin and the method of extraction. For each tonne of product, approximately an equal tonnage of bauxite residue is produced (Pera et al. 1997; Zhang et al. 2011), this equates to over 120 million tons per year globally (Power et al. 2011a). This bauxite residue is highly caustic and can contain high levels of heavy metals depending on the origin of the bauxite. For this reason red mud is difficult to dispose of and in 2011 it was reported that 2.7 billion tons were currently stored in land-based repositories globally (Power et al. 2011a; Zhang et al. 2014). In 2010, at the Ajka aluminium works in Hungary, excess rainfall caused a corner of the reservoir where the waste was being stored to collapse releasing approximately 700,000 m<sup>3</sup> of the caustic liquid waste which subsequently killed 10 people, injured many more and caused considerable environmental damage (Gelencér et al. 2011; Mayes et al.

2011; Ruyters et al. 2011; Burke et al. 2013). This disaster has raised awareness of the red mud waste issue and has led to several investigations on how to reuse it in secondary materials (Power et al. 2011b). There have been some recent publications investigating these reuse options, such as in Portland cement production, brick manufacturing and road building, although they have reportedly been associated with limitations due to high alkalinity, efflorescence and transporting costs (Liu et al., 2014). Developments of sintered ceramics with red mud fly ash mixture have also been reported (Ponsot et al., 2015, Samal et al., 2015). However in this study we aim to determine the feasibility of utilising bauxite residue in the manufacture of lightweight aggregate and determine the possible quantities that PFA can be substituted by red mud. This is a completely novel approach and has huge potential for a wide use of different applications depending on the properties achieved after pelletising and firing.

#### 2. Materials and Methods

The bauxite residue under test was from China, where it is estimated that more than 70 million tonnes are produced annually (Liu *et al.* 2009). Sewage sludge was selected as a fuel as it is a semi-solid waste material that is becoming increasing difficult to dispose of (Ødegaard et al. 2002; Fytili and Zabaniotou; 2008), yet will ensure that a lightweight aggregate is produced once fired. All materials used in the aggregate production where locally sourced from the Chongqing municipality, China. The bauxite residue was from the NanChuan Alumina Plant, the PFA from the LuoHuang Power Station, the sewage from the JiGuanShi Sewage Treatment Plant and the clay from the DaDuKou District.

Optimal combinations of PFA, clay and dewatered sewage sludge have previously been reported by Wen-fa Tan *et al.* (2012) and were used in this study. The PFA was replaced by bauxite residue on a 1:1 dry weight ratio, from a quarter to half the amount in the following percentage ratios: 25, 31, 38, 44 and 50 %. These ratios were chosen based on previous investigations by Trefoil Technology Ltd. (unpublished data) which showed that replacement of PFA above 50 % greatly reduced the quality and strength of the aggregate.

#### 2.1 Aggregate Production

A pilot plant supplied by RTAL China Ltd. to produce lightweight aggregate using the Trefoil Rotary kiln was set up at the University of Chongqing, China. This kiln is made of incaloy and has a length of 0.8 m and a diameter of 0.2 m and is ideal for using problematic wastes in aggregate production due to its superior thermal efficiency (Wainwright and Cresswell, 2001), its compliance with required emission standards and cost efficiency.

The manufacturing procedure followed that described by Sarabèr et al. (2012) – in brief the waste materials were mixed together and granulated with a drum granulator. 15 kg (wet weight) of each replacement percentage mix (25, 31, 38, 44 and 50 %) was prepared and pelletised to sizes ranging from 4mm to 16mm. These 'green pellets' were then dried in a conventional oven at 105 °C overnight until they reached constant weight. Approximately half the pellets from each of the five replacement ratios were left unfired, whilst the rest were fed into the Trefoil kiln at 500 °C and fired to 1200 °C. The pellets were fired in 3-4 kg batches for 25 minutes at a rotation speed of 7-8 rpm. After production a random sample of 5 kg of unfired pellets and 5 kg of fired pellets were selected for each of the five replacement ratios for aggregate characterisation.

#### 2.2 Aggregate physical characterisations

#### 2.2.1 Aggregate strength

To determine the strength of the five different aggregates from the fired group, the pin crusher test was used (as in Saraber *et al.* 2012 and similar to that described by Cheeseman *et al.* 2005). Samples of 20 aggregate pieces were randomly selected from each fired replacement group and put into a pin crusher. The pin was tightened until the aggregate fractured and the force (in MPa) required to cause the break was recorded.

#### 2.2.2 pH Values and Conductivity

The pH was determined for the five aggregate types before and after firing. Each had twelve replicates, therefore there were 120 samples in total. 30 g of material was soaked in 75 ml of distilled water, stirred and left for 24 h, then three readings using a YSI proplus multiparameter meter were taken for each sample to get an accurate mean for each of the replicates. The conductivity was tested at the same time as pH with the multipurpose meter probe. Mean values were recorded as  $\mu$ S/cm.

#### 2.2.3 Particle Density and Water Absorption

The particle density and water absorption of the fired aggregates were characterised according to BS EN 1097-6 2000. Particle density was determined using 500 g samples of aggregate and each replicated three times (15 samples in total). Particle density was

then calculated in Mg/m<sup>3</sup> using the weight of: the saturated surface dried aggregate (W1), the container with saturated aggregate and water (W2), the container alone filled with water (W3) and the weight of the oven dried aggregate (W4), using the following equation:

Particle Density = 
$$\frac{\text{density of water x W4}}{W4 - (W2 - W3)}$$

Water absorption capacity (%) was calculated using the weight of the saturated surface dried aggregate (W1) and the oven-dried aggregate (W4) using the following equation:

Water Absorption = 
$$100 \ge \frac{(W1 - W4)}{W4}$$

#### 2.2.4 Bulk Density

The loose bulk density of each of the five fired aggregate samples, was characterised using BS EN 1097-3:1998. To measure loose bulk density an empty container (11 capacity) was weighed and then reweighed once filled with the test sample. This was repeated three times for each aggregate and the loose bulk density calculated in Mg/m<sup>3</sup>.

#### 2.3 Aggregate chemical characterisations

#### 2.3.1 XRF Oxide Composition Analysis

X-ray fluorescence analysis (XRF) that determines elemental oxide percentages was carried out at the University of Greenwich using a Philips PW1400 XRF. The five different aggregates in both the unfired and fired groups were subjected to standard XRF testing following XRF Scientific Ltd. guidelines for selected elements, including; Al, Ca, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, P, Rb, S, Si, Sr, Ti, Zn and Zr.

#### 2.3.2 Leachate analysis

Metal leachates were analysed from the five unfired and five fired aggregate types using inductively coupled plasma atomic emissions spectrometry (ICP-AES). The testing procedure from BS EN 12457-3:2002 was followed where 20 g of each aggregate (replicated three times) and 40 ml of distilled water were placed in bottles onto a rotating turntable and left for 6 h, filtered then rotated for a further 18 h. Whattman 0.45#m CA w/GMF disposable housing with filters were used for sample extractions that were then run through a Perkin Elmer Instrument, Otima 4300 DV for analysis. Elements of particular interest included: Al, Ba, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Sr, Ti and Zn.

#### 2.4 Statistical Analysis

Results for material characterizations were analysed where possible – to detect differences between the five aggregate types (replacement of PFA with red mud in ratios of 25, 31, 38, 44 and 50 %) and between aggregates before and after firing – using one-way analysis of variance (ANOVA) (Zar, 2005). Means were separated with a Tukey's HSD post hoc test (Fowler, 1998). Data were tested for normality and transformed using log or square root when appropriate. However for leachate data, metal concentrations were compared between unfired and fired groups using paired T-test or the non-parametric Wilcoxon signed ranks where data could not be normalised. All analyses were conducted using the statistical package SPSS v. 20.0.

#### 3. Results

A sample of the aggregates produced in this experiment can be seen in Figure 1. There is little visual difference in the aggregate produced with the differing ratios of red mud to PFA. The friability of the fired products was also very similar with the highest red mud replacement percentage producing a successful product with no fractures.

#### 3.1 Aggregate physical characterisations

#### 3.1.1 Individual pellet strength test

There were significant differences,  $F_{(4, 375)} = 10.95$ , P < 0.001, in the force that could be applied to individual pellets before they fractured and broke apart – this ranged from 6 MPa to 8 MPa. However, these differences did not correlate with changes in red mud to PFA ratio. In fact, the aggregate with 44% red mud replacement required the greatest applied force to break while the aggregate with 50% red mud replacement required the least (Figure 2).

#### 3.1.2 pH Values and Conductivity

Before firing, the pH of all the pellets was approximately 11 and this reduced to around 8 after firing (Figure 3). The differences in pH values of the pellets before firing was significant,  $F_{(4, 55)} = 543.62$ , P < 0.001, with the 25 % and 50 % red mud replacement having significantly higher pH values than the middle three percentages. Nevertheless, there was no significant difference in pH in any of the replacement ratios after firing.

The conductivity of all the pellets was drastically reduced after firing, from above  $3000 \ \mu$ S/cm to below 500  $\mu$ S/cm. There were significant differences between the ratios of

red mud replacement before firing,  $F_{(4, 55)} = 46.97$ , P < 0.001 and after firing,  $F_{(4, 55)} = 24.97$ , P < 0.001, where in both cases the 25, 31 and 38 % were significantly lower than the larger replacement ratios.

#### 3.1.3. Particle Density, Bulk Density and Water Holding Capacity

Table 1 shows the results from the aggregate characterisations. The red mud replacement percentage of 44 % had the largest water absorption (6.26 %) and the highest particle, apparent and loose bulk densities. However in general, there was a slight upward trend in all measured results with increasing amounts of red mud replacement. The void space percentage within the pellets were the only results that did not follow this pattern, all results were very similar at around 40 - 42 %.

#### 3.2 Aggregate chemical characterisations

## 3.2.1 XRF Oxide Composition Analysis

As the amount of red mud in the pellets increased so did the amounts of Na<sub>2</sub>O and Fe<sub>2</sub>O<sub>3</sub> in both the unfired and fired pellets. Conversely, the amounts of SiO<sub>2</sub> and CaO decreased with increasing red mud concentration in the unfired and fired pellet groups. There was a small but generally increasing trend in the amount of TiO<sub>2</sub> once the aggregates were fired, and a small but generally decreasing trend in the amount of K<sub>2</sub>O from both the unfired and fired pellets. Finally for Al<sub>2</sub>O<sub>3</sub>, MgO, MnO and P<sub>2</sub>O<sub>5</sub> there were similar levels between the red mud to PFA ratios before firing and similarly after firing, no real pattern was observed.

#### 3.2.2 Leachate analysis

The metal leachates recorded for both the unfired and fired aggregates are listed in Table 3. There were significant reductions post-firing for: aluminium leachates,  $t_{(28)} = 7.57$ , P < 0.001; iron,  $t_{(28)} = 11.54$ , P < 0.001; phosphorus, Z = 4.67, P < 0.001; potassium, Z = 0.67, P < 0.001; sodium, Z = 4.67, P < 0.001 and sulphur, Z = 4.67, P < 0.001. Whilst magnesium and zinc leachates were significantly increased post-firing; Z = 4.67, P < 0.001 and Z = 4.680, P < 0.001 respectively.

There were significant differences in leachates between the red mud replacement ratios in the unfired group for; aluminium,  $F_{(4, 10)} = 13.940$ , P < 0.001; calcium,  $F_{(4, 10)} = 21.701$ , P < 0.001; iron,  $F_{(4, 10)} = 21.701$ , P < 0.001; magnesium,  $\chi^2_{(4)} = 10.850$ , P < 0.05; phosphorus,  $\chi^2_{(4)} = 12.433$ , P < 0.01; potassium,  $\chi^2_{(4)} = 12.704$ , P < 0.01; sodium,  $\chi^2_{(4)} = 11.700$ , P < 0.05 and sulphur,  $\chi^2_{(4)} = 9.904$ , P < 0.05. Yet there were no significant differences between the percentages of red mud in the fired groups, except for phosphorus, and zinc where  $\chi^2_{(4)} = 12.422$ , P < 0.01 and  $\chi^2_{(4)} = 12.900$ , P < 0.01 respectively.

The most common pattern observed was that leachates were increased with increasing red mud replacement in both the unfired and fired aggregate groups, although the levels tended to be considerably lower once firing had taken place.

#### 4. Discussion

#### 4.1 Physical characterisations

The results of this study demonstrate that red mud can be utilised for the production of lightweight aggregate, even with up to 50 % replacement of PFA (on a 1:1 dry weight ratio). Previous work by Blank (1976) found that aggregate manufactured using bauxite residue did not produce a lightweight aggregate, despite only including around 10% of the total dry weight and testing several different additives to the green pellets. However our on-going research (unpublished data) suggests that these volumes could actually reach 30 % dry weight before the aggregate becomes too heavy to be classified as lightweight.

The crushing strength of the material produced ranged from 6 – 8 MPa. This strength is slightly lower than a comparative lightweight material such as Lytag, which has a crushing value of 14.9 MPa (Wassermann & Bentur 1997), yet it is still within ranges produced by other manufactured aggregates using sewage sludge (Cheeseman & Virdi 2005). The results showed that at around 44 % red mud replacement, the aggregate reached an optimal strength and after this (as shown with 50 % replacement) the aggregates were at their weakest. In general, compressive strength of aggregates is affected by a number of inter-relating physical and chemical parameters. Oxide compositions of raw materials, the nature of newly formed crystal phase (due to sintering), pore structure, pore distribution and density play an important role in the compressive strength of sintered aggregates (Lin, 2006, González-Corrochano et al., 2011). However, in this study, changes in strength of aggregates produced under the same sintering conditions (i.e. temperature and firing time), suggests the significant influence of oxide compositions. Therefore, the highest compressive strength for 44% of red mud

could be correlated to its lower porosity (due to its low level of silicate phase) and to its high density (Tsai et al., 2006).

The pH values of all the material was drastically reduced after the aggregates were fired, decreasing from approximately pH 11 to pH 8, yet there were no significant differences between the various ratio replacements. The materials' before and after firing results indicate that thermal processing chemically alters the aggregates and shows content of red mud within the mixes is not a significant factor affecting the final pH value. Likewise the green pellet conductivity is significantly higher than that from postfired material. This again highlights the effect of thermal processing on the chemical properties of the aggregate. The reduction in pH and conductivity is especially important for a growing media application (Molineux et al. 2009), as many plant species cannot tolerate pH values above 8 (Day & Ludeke 1993).

For other characterisation data, including bulk density, particle density and water holding capacity – the 44 % red mud replacement of PFA resulted in the largest values. Despite these pellets being the heaviest, they also absorbed the highest amount of water, which is surprising as their densities suggest that the structure may contain fewer air spaces than the lighter material. The larger capacity to absorb water may then be due to the internal structure of theses pores within the aggregate (Cheesman & Virdi 2005). The concentration of silicate-base minerals in the aggregates structure will affect the viscosity of the glass phase during the firing process. A glass phase with higher viscosity can capture more gas, thus producing a material with increased porosity (de' Gennaro et al., 2004). The aggregates tested in this study may have had an insufficient viscosity (due to low concentrations of silicate components) that would, in turn, affect their density. A lower silicate phase will result in less expansion and thus produce a material of higher density. The different particle densities for each proportion of red mud in aggregates could therefore be a result of differences in materials' expansion and/or changes in materials density upon heating (Wasserman and Bentur, 1997). However the influences of the latter was considered to be very low, since each type of aggregate had been produced under the same firing conditions (i.e. temperature and resident time). In respect of the 44 % bauxite residue replacement, the increased capacity to hold water may also have been due to the severe decrease in concentration of Fe<sub>2</sub>O<sub>3</sub> during firing – a result of oxidationreduction reaction of ferric oxides (Chiou et al., 2006). That reaction generates a sudden release of an excessive amount of gas producing an open pore network with pathways to surface without affecting the density.

#### 4.2 Chemical characterisations

The results of oxide composition analysis (XRF) of unfired and fired pellets are shown in Table 2. Most oxide levels in the bauxite residue are within the parameters previously described by Gräfe et al. (2009), where values documented are fairly wide-ranging due to red mud being chemically different from region to region and also due to the bauxite quality and process of alumina extraction (Pontikes & Angelopoulos 2013). However in our bauxite residue, silicon oxide content was considerably higher than the mean from the Gräfe et al. (2009) study – around 40 % compared to 10 % respectively. The normalized compositions were therefore plotted in a ternary diagram (Figure 5.) in order to evaluate their expansion capability during the firing (sintering) process according to requirements presented in the literature (Riley 1951). Low SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>/flux (Fe<sub>2</sub>O<sub>3</sub> + CaO +  $MgO + Na_2O + K_2O$ ) ratios suggest that the materials had poor expandability and were positioned out of bloating area.

The results from the leachates testing have shown that although the levels of metals from the unfired green pellets were high, post-firing levels all ranged within acceptable levels for the European landfill directive (2003/33/EC). The levels of phosphorous and zinc were the only leachates that significantly differed between the five percentages of red mud replacement - with the 44 % replacement again being the lowest and thus seeming to be the optimal quantity. Bauxite residue is known to have caustic properties, a result of high levels of heavy metals and a high pH value. This study has shown that pelletisation and thermal processing 'locks-up' these contaminants and decreases the materials pH, stabilizing some of the inorganic components in the solid body and thus, hindering their leachability in water (Sivula et al., 2010, Fuente-Cuesta et al., 2013). This trend was evident for aluminium, iron, phosphorus, potassium, sodium and sulphur. Al is an amphoteric metal that shows high solubility under extreme basic and acidic conditions (Sabbas et al., 2003). That could explain the decrease in Al leaching behaviour as a consequence of pH drop to a more natural range. The pH dependency for leaching of other elements was in accordance with V-shape solubility curves indicated in literature, since low solubility was observed at pH range 7 – 8 (Gori et al., 2011; Dijkstra et al., 2006). In an opposite trend, the concentration of Zn and Mg significantly increased with the drop in pH caused by the firing process. This was in agreement with previous studies (Dijkstra et al., 2002; van der Sloot et al., 2001).

#### 5. Conclusion

The potential for the manufacture of lightweight aggregates from problematic wastes, such as red mud, has been demonstrated here. Aggregates produced in this way are recycling material otherwise difficult to store/dispose of and could provide secondary products of value. From this study the following conclusions can be drawn:

- 44 % red mud replacing the PFA content of the aggregate mix produced the most favourable values for the characteristics analysed.
- The produced aggregates demonstrated high water absorption capacity, which makes them suitable for urban greening applications.
- The high water absorption was also evident for aggregates with high density that may be attributed to their open pore structure as the result of gases released at high temperatures.
- The concentrations of heavy metals in prepared leachates for the fired pellets were below regulatory target limits.

To take this work forward, future investigations should focus on the bauxite residue replacement around the 40 % - 50 % range and should test the crystallography and pozzolanic characteristics of the fired aggregates. Quenching could also be investigated to determine if suitable (lower water holding capacity) products could be manufactured for use in concretes and other construction-based applications. This research has shown a potential reuse option for a large percentage of red mud replacement of PFA. A full technical and economic feasibility study on

commercial scale production can now be taken forwards and future studies would hopefully impact not only regionally in China but also internationally.

#### 6. Acknowledgements

We are grateful to Terry Green at Trefoil Technology Ltd. for technical expertise in manufacturing lightweight aggregate and to Silvia Lai for her time organising data collected. We are also thankful to Cradle 2 Cradle for post-analysis funding and to the anonymous reviewers of this manuscript for their positive and constructive feedback.

#### References

- (2003/33/EC) COUNCIL DECISION of 19 December 2002 establishing criteria and procedures for the acceptance of waste at landfills pursuant to Article 16 of and Annex II to Directive 1999/31/EC.
- Ahmaruzzaman, M. (2010). A review on the utilization of fly ash. Progress in Energy and Combustion Science 36: 327–363.
- Aineto, M., Acosta, A., Rincón, J. & Romero, M. (2005). Production of lightweight aggregates from coal gasification fly ash and slag. World of Coal Ash (WOCA), April 11-15, Lexington, Kentucky.
- Blank, H. R. (1976). Red Mud from Alumina Plants as a Possible Source of Synthetic Aggregate. Journal of Testing and Evaluation. 4(5): 355-358.

- Burke, I. T., Mayes, W. M., Peacock, C. L., Brown, A. P., Jarvis, A. P. & Gruiz, K.
  (2012). Speciation of Arsenic, Chromium, and Vanadium in Red Mud Samples from the Ajka Spill Site, Hungary. Environmental Science and Technology. 46: 3085–3092.
- Burke, I. T., Peacock, C. L., Lockwood, C. L., Stewart, D. I., Mortimer, R. J. G., Ward,
  M. B., Renforth, P., Gruiz, K. & Mayes, W. M. (2013). Behaviour of Aluminium,
  Arsenic, and Vanadium during the Neutralization of Red Mud Leachate by HCl,
  Gypsum, or Seawater. Environmental Science and Technology. 47: 6527–6535.
- BS EN 1097-3 (1998). Tests for mechanical and physical properties of aggregates. Part3: Determination of loose bulk density and voids. ISBN 0 580 30086 2.

BS EN 1097-6 (2000). Tests for mechanical and physical properties of aggregates.

Determination of particle density and water absorption. ISBN 0 580 36056 3.

- BS EN 12457-3 (2002). Characterisation of waste. Leaching. Part 3: Compliance test for leaching of granular waste materials and sludges. Two stage batch test at a liquid to solid ratio of 2 l/kg and 8 l/kg for materials with a high solid content and with a particle size below 4mm (without or with size reduction). ISBN 0 580 40581 8.
- Chang, F.-C., Lo, S.-L., Lee, M.-Y., Ko, C.-H., Lin, J.-D., Huang, S.-C. & Wang, C.-F. 2007. Leachability of metals from sludge-based artificial lightweight aggregate. *Journal of Hazardous Materials*, 146, 98-105.
- Cheeseman, C. R., Makinde, A., & Bethanis, S. (2005). Properties of lightweight aggregate produced by rapid sintering of incinerator bottom ash. Resources, Conservation and Recycling. 43: 147-162.

- Cheeseman, C. R. & Virdi, G. S. (2005). Properties and microstructure of lightweight aggregate produced from sintered sewage sludge ash. Resources, Conservation and Recycling. 45: 18-30.
- Chiou, I.-J., K.-S. Wang, C.-H. Chen, and Y.-T. Lin. (2006). Lightweight aggregate made from sewage sludge and incinerated ash. Waste Management 26:1453-1461.Day & Ludeke (1993).
- de' Gennaro, R., P. Cappelletti, G. Cerri, M. de' Gennaro, M. Dondi, and A. Langella.(2004). Zeolitic tuffs as raw materials for lightweight aggregates. Applied Clay Science 25:71-81.
- Dijkstra, J. J., H. A. van der Sloot, and R. N. J. Comans. (2002). Process identification and model development of contaminant transport in MSWI bottom ash. Waste Management 22:531-541.
- Dijkstra, J. J., H. A. van der Sloot, and R. N. J. Comans. (2006). The leaching of major and trace elements from MSWI bottom ash as a function of pH and time. Applied Geochemistry 21:335-351.
- Fowler, J., Cohen, L., & Jarvis, P. (1998). Practical Statistics for Field Biology. Second edition. John Wiley & Sons.
- Francis, R. A. & Lorimer, J. (2011). Urban reconciliation ecology: The potential of living roofs and walls. Journal of Environmental Management. 92: 1429-1437.
- Fuente-Cuesta, A., M. A. Lopez-Anton, M. Diaz-Somoano, A. v. Zomeren, M. Cieplik, and M. R. Martínez-Tarazona. (2013). Leaching of major and trace elements from paper–plastic gasification chars: An experimental and modelling study. Journal of Hazardous Materials 244–245:70-76.

- Fytili, D. & Zabaniotou, A. (2008). Utilization of sewage sludge in EU application of old and new methods – A review. Renewable and Sustainable Energy Reviews. 12: 116-140.
- Gelencsér, A., Kováts, N., Turóczi, B., Rostási, A., Hoffer, A., Imre, K., Nyirő-Kósa, I.,
  Csákberényi-Malasics, D., Tóth, A., Czitrovszky, A., Nagy, A., Nagy, S., Ács, A.,
  Kovács, A., Ferincz, A., Hartyáni, Z. & Pósfai, M. (2011). The Red Mud Accident
  in Ajka (Hungary): Characterization and Potential Health Effects of Fugitive
  Dust. Environmental Science and Technology. 45(4): 1608–1615.
- González-Corrochano, B., J. Alonso-Azcárate, M. Rodas, J. F. Barrenechea, and F. J. Luque. (2011). Microstructure and mineralogy of lightweight aggregates manufactured from mining and industrial wastes. Construction and Building Materials 25:3591-3602.
- Gori, M., L. Pifferi, and P. Sirini. (2011). Leaching behaviour of bottom ash from RDF high-temperature gasification plants. Waste Management 31:1514-1521.
- Gràfe, M., Power, G. & Klauber, C. (2009). Review of bauxite residue alkalinity and associated chemistry. CSIRO Document DMR-3610, Project ATF-06-3: "Management of Bauxite Residues". Department of Resources, Energy and Tourism (DRET).
- Hwang, C. L., Bui, L. A. T., Lin, K. L. & Lo, C. T. (2012). Manufacture and performance of lightweight aggregate from municipal solid waste incinerator fly ash and reservoir sediment for self-consolidating lightweight concrete. Cement and Concrete Composites. 34(10): 1159–1166.

Kourti, I. & Cheeseman, C. R. (2010). Properties and microstructure of lightweight

aggregate produced from lignite coal fly ash and recycled glass. Resources, Conservation and Recycling. 54: 769–775.

- Laursen, K., White, T. J., Cresswell, D. J. F., Wainwright, P. J. & Barton, J. R. (2006). Recycling of an industrial sludge and marine clay as lightweight aggregates. Journal of Environmental Management. 80: 208–213.
- Liaw, C. T., Chang, H. L., Hsu, W. C. & Huang, C. R. (1998). A novel method to reuse paper sludge and co-generation ashes from paper mill. Journal of Hazardous Materials. 58: 93–102.
- Lin, K. (2006). Mineralogy and microstructures of sintered sewage sludge ash as lightweight aggregates. JOURNAL OF INDUSTRIAL AND ENGINEERING CHEMISTRY-SEOUL- 12:425.
- Liu, W., Yang, J. & Xiao, B. (2009). Review on treatment and utilization of bauxite residues in China. International Journal of Mineral Processing. 93: 220–231.
- Liu, W., Chen, X., Li, W., Yu, Y. & Yan, K. 2014. Environmental assessment, management and utilization of red mud in China. *Journal of Cleaner Production*, 84, 606-610.
- Mayes, W. M., A. P. Jarvis, I. T. Burke, M. Walton, V. Feigl, O. Klebercz, and K. Gruiz.
  (2011). Dispersal and attenuation of trace contaminants downstream of the ajka bauxite residue (Red Mud) depository failure, Hungary. Environmental Science and Technology 45:5147-5155.
- Molineux C. J., Fentiman, C. H. & Gange, A. C. (2009). Characterising alternative recycled waste materials for use as green roof growing media in the U.K. Ecological Engineering. 35: 1507–1513.

- Molineux, C. J., Connop, S. P. & Gange, A.C. (2014). Manipulating soil microbial communities in extensive green roof substrates. Science of the Total Environment 493: 632-638.
- Ødegaard, H., Paulsrud, B. & Karlsson, I. (2002). Wastewater sludge as a resource: sludge disposal strategies and corresponding treatment technologies aimed at sustainable handling of wastewater sludge. Water Science & Technology. 46(10): 295–303.
- Owens, P. L. (1993). Lightweight aggregates for structural concrete. Structural Lightweight Aggregate Concrete. 1–18.
- Pera, J., Boumaza, R., & Ambroise, J. (1997). Development of a pozzolanic pigment from red mud. Cement and Concrete research. 27(10): 1513-1522.
- Pioro, L. S. & Pioro, I. O. (2004). Production of expanded-clay aggregate for lightweight concrete from non-selfbloating clays. Cement and Concrete Composites. 26: 639-643.
- Pontikes, Y., and G. N. Angelopoulos. (2013). Bauxite residue in cement and cementitious applications: Current status and a possible way forward. Resources, Conservation and Recycling 73:53-63.
- Ponsot, I., Bernardo, E., Bontempi, E., Depero, L., Detsch, R.,
  Chinnam, R. K. & Boccaccini, A. R. 2015. Recycling of pre-stabilized municipal waste incinerator fly ash and soda-lime glass into sintered glass-ceramics. *Journal of Cleaner Production*, 89, 224-230.
- Power, G., Gràfe, M. & Klauber, C. (2011a). Bauxite residue issues: I. Current management, disposal and storage practices. Hydrometallurgy. 108(1): 33-45.

- Riley, C. M. (1951). Relation of Chemical Properties to the Bloating of Clays. Journal of the American Ceramic Society 34:121-128.
- Ruyters, S., Mertens, J., Vassilieva, E., Dehandschutter, B., Poffijn, A. & Smolders, E.
  (2011). The Red Mud Accident in Ajka (Hungary): Plant Toxicity and Trace Metal Bioavailability in Red Mud Contaminated Soil. Environmental Science and Technology 45(4): 1616–1622.
- Sabbas, T., A. Polettini, R. Pomi, T. Astrup, O. Hjelmar, P. Mostbauer, G. Cappai, G.
  Magel, S. Salhofer, C. Speiser, S. Heuss-Assbichler, R. Klein, and P. Lechner.
  (2003). Management of municipal solid waste incineration residues. Waste Management 23:61-88.
- Samal, S., Ray, A. K. & Bandopadhyay, A. 2015. Characterization and microstructure observation of sintered red mud–fly ash mixtures at various elevated temperature. *Journal of Cleaner Production*, 101, 368-376.
- Sarabèr, A., Overhof, R., Green T. & Pels, J. (2012). Artificial lightweight aggregates as utilization fur future ashes A case study. Waste Management 32: 144-152.
- Sivula, L., A. Ilander, A. Väisänen, and J. Rintala. (2010). Weathering of gasification and grate bottom ash in anaerobic conditions. Journal of Hazardous Materials 174:344-351.
- Swamy, R. N., and G. H. Lambert. (1981). The microstructure of Lytag aggregate. International Journal of Cement Composites and Lightweight Concrete 3:273-282.
- Tang, C. W., Chen, H. J., Wang, S. Y. & Spaulding, J. (2011). Production of synthetic

lightweight aggregate using reservoir sediments for concrete and masonry. Cement and Concrete Composites. 33: 292–300.

- Tsai, C.-C., K.-S. Wang, and I.-J. Chiou. (2006). Effect of SiO2–Al2O3–flux ratio change on the bloating characteristics of lightweight aggregate material produced from recycled sewage sludge. Journal of Hazardous Materials 134:87-93.
- Terukina, J., Kumamoto, J. & Kinari, H. (1993). Manufacturing of artificial lightweight aggregate utilizing coal fly ash. Tokyo: Ecomaterials.
- Van der Sloot, H. A., Kosson, D. S., & Hjelmar, O. (2001). Characteristics, treatment and utilization of residues from municipal waste incineration. Waste Management. 21(8): 753-765.
- Wainwright, P. J., & Cresswell, D. J. F. (2001). Synthetic aggregates from combustion ashes using an innovative rotary kiln. Waste Management. 21: 241-246.
- Wasserman, R., and A. Bentur. (1997). Effect of lightweight fly ash aggregate microstructure on the strength of concretes. Cement and Concrete Research 27:525-537.
- Zar, J. H. (2005). Biostatistical Analysis, Pearson Education, Upper Saddle River, NJ.
- Zhang, N., Liub, X., Sunc, H., & Li, L. (2011). Evaluation of blends bauxite-calcinationmethod red mud with other industrial wastes as a cementitious material: Properties and hydration characteristics. Journal of Hazardous Materials. 185: 329-335.
- Zhang, M., El-Korchi, T., Zhang, G., Liang, J. & Tao, M. (2014). Synthesis factors affecting mechanical properties, microstructure and chemical composition of red mud–fly ash based geopolymers. Fuel. 134: 315-325.

Characteristic	Red Mud (%) substituted for PFA in Pellets							
Characteristic	25	31	38	44	50			
Water Absorption (%)	5.16	5.23	5.13	6.26	6.02			
	(0.38)	(0.38)	(0.39)	(0.19)	(0.23)			
Particle Density – Dry (Mg/m <sup>3</sup> )	1.64	1.63	1.69	1.71	1.65			
	(0.01)	(0.04)	(0.03)	(0.02)	(0.02)			
Particle Density – Wet (Mg/m <sup>3</sup> )	1.73	1.72	1.77	1.83	1.76			
	(0.01)	(0.03)	(0.02)	(0.02)	(0.02)			
Apparent Density (Mg/m <sup>3</sup> )	1.81	1.79	1.85	1.94	1.86			
	(0.01)	(0.05)	(0.02)	(0.03)	(0.02)			
Loose Bulk Density (Mg/m <sup>3</sup> )	0.94	0.96	0.97	0.99	0.97			
	(0.01)	(0.01)	(0.01)	(0.01)	(0.01)			
Compacted Bulk Density (Mg/m <sup>3</sup> )	1.03	1.03	1.04	1.07	1.06			
	(0.01)	(0.01)	(0.02)	(0.02)	(0.01)			
Void Space (%)	42.5	40.8	42.4	42.0	41.3			
	(0.78)	(1.38)	(0.55)	(0.68)	(0.60)			

 Table 1. Characterization of aggregate with increasing red mud content.

Data represent the mean and  $\pm$  the standard error.

			Red N	/Iud (%)	substitu	uted for PFA in Pellets				
Element Oxide (%)	Unfired					Fired				
	25	31	38	44	50	25	31	38	44	50
$Al_2O_3$	15.27	15.21	14.20	14.29	16.30	18.50	17.37	18.34	18.15	17.63
CaO	4.48	4.27	3.74	3.53	3.84	4.60	4.36	4.36	4.17	4.03
Fe <sub>2</sub> O <sub>3</sub>	20.14	21.46	28.66	29.46	24.47	20.65	21.95	22.62	23.75	24.67
$K_2O$	1.61	1.55	1.42	1.42	1.53	1.62	1.59	1.60	1.57	1.55
MgO	1.06	0.96	1.18	1.14	1.16	1.57	1.28	1.53	1.45	1.45
MnO	0.12	0.12	0.28	0.28	0.13	0.12	0.13	0.13	0.13	0.13
Na <sub>2</sub> O	2.74	2.96	3.05	3.46	4.09	1.94	2.05	2.55	2.81	3.03
$P_2O_5$	0.67	0.60	0.59	0.60	0.65	0.37	0.33	0.40	0.40	0.41
$SiO_2$	32.59	30.55	28.21	27.22	29.89	43.75	40.13	41.84	40.05	38.99
TiO <sub>2</sub>	2.48	2.57	2.22	2.24	2.61	2.57	2.60	2.61	2.62	2.62

**Table 2**. XRF analysis showing elemental composition from unfired and fired aggregate, made with increasing percentage of red mud substitute.

	Red Mud (%) substituted for PFA in Pellets											
Lechate (ppm) —		Fired										
	25	31	38	44	50	25	31	38	44	50		
Aluminium*	8.36 a	6.79 a	11.46 ab	15.49 b	18.52 bc	0.55	0.46	2.10	1.02	3.26		
Arsenic	0.05	0.06	0.07	0.08	0.09	0.04	-	-	-	-		
Barium	-	-	-	-	-	0.02	0.03	0.02	0.03	0.03		
Cadium	-	-	-	-	- 2	0.01	-	-	0.01	-		
Calcium*	12.20 a	3.60 b	3.40 b	3.12 b	2.45 b	6.65	4.53	4.63	5.35	5.93		
Chromium	0.02	0.02	0.02	0.02	0.02	-	-	-	-	-		
Cobalt	0.02	0.02	0.02	0.02	0.02	-	-	-	-	-		
Copper	0.62	0.65	0.60	0.70	0.64	-	-	-	-	-		
Iron*	0.99 a	1.13 ab	1.46 bc	1.48 c	1.91 d	0.14	0.11	0.19	0.11	0.32		
Lead	-	-	- 🖂	×-	-	-	-	-	-	-		
Lithium	0.04	0.03	0.03	0.03	0.02	0.04	0.02	0.05	0.02	0.02		
Magnesium <sup>†</sup>	0.03 ac	0.05 b	0.04 a	0.03 c	0.03 ac	0.88	0.25	0.67	0.82	1.43		
Manganese	-	-		0.01	0.01	0.02	0.02	0.03	0.02	0.03		
Nickel	0.08	0.09	0.07	0.07	0.08	-	-	-	-	-		
Phosphorus†	1.91 a	3.28 b	4.01 bc	3.15 ab	4.43 c	0.26 a	0.10 b	0.09 b	0.00 c	0.00 c		

Potassium†	18.09 a	18.40 a	21.01 b	22.26 bc	26.06 c	0.58	0.55	0.83	0.90	1.27
Sodium†	228.42 a	253.22 b	279.14 c	292.49 d	338.16 e	6.58	6.43	9.30	13.32	15.62
Strontium	0.07	0.02	0.02	0.01	0.01	0.05	0.04	0.04	0.04	0.05
Sulphur†	108.74 a	113.48 b	128.01 c	106.58 a	108.39 a	6.96	5.76	6.42	11.41	10.53
Titanium	0.02	0.04	0.05	0.06	0.09	-	-	-	-	-
Vanadium	0.13	0.16	0.18	0.22	0.24	5	-	-	-	-
Zinc†	0.02	0.02	0.02	0.02	0.02	0.50 a	0.29 b	0.27 b	0.08 c	0.86 d

Table 3. Metal leachates from unfired and fired aggregate, made with increasing percentage of red mud substitute. Analysed by ICP-AES.\* indicates data normally distributed, whilst † indicates non-parametric data from unfired and fired groups. Light grey highlights a significant reduction inleachates after firing; conversely dark grey highlights a significant increase in leachate after firing. Means analysed with ANOVA or Kruskal-Wallis test anddifferences separated with Tukey HSD or t-tests. Values not sharing the same letter indicate a significant difference (P <0.05).</td>

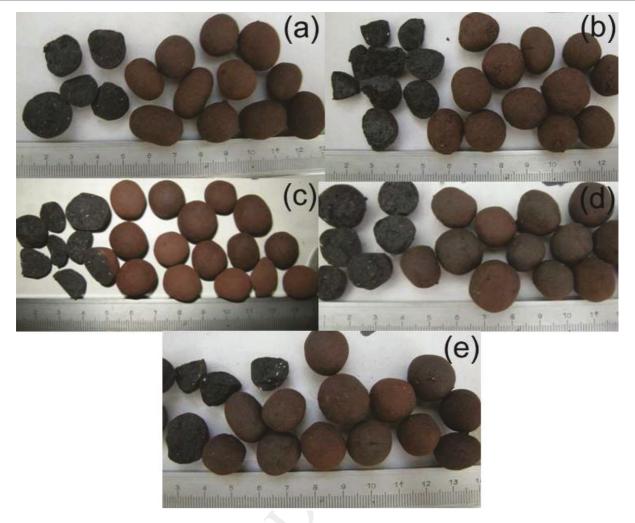
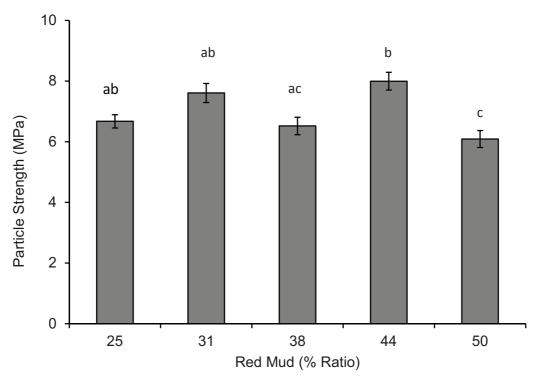


Figure 1. Fired aggregate photographs of the pellets containing increasing red mud. (a) 25%, (b) 31%, (c) 38%, (d) 44%, (e) 50%. On the left of each of the photos are broken aggregate pellets, used for the strength test, that reveal the internal structure of the pellets.



**Figure 2.** Strength of aggregate with reduction in PFA and increase in red mud content. Means analysed with ANOVA and differences separated with Tukey HSD. Values not sharing the same letter indicate a significant difference (P < 0.05). Bars represent means  $\pm$  one standard error.

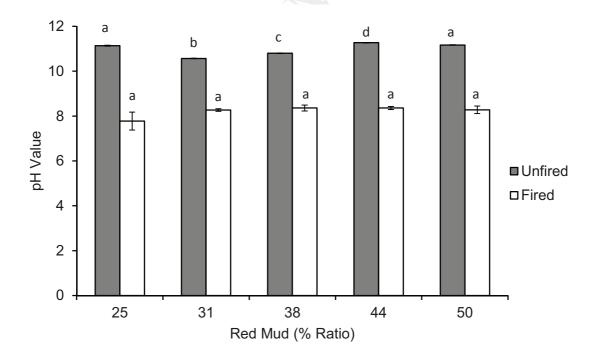


Figure 3. pH of aggregates before and after sintering. Means analysed with ANOVA and differences separated with Tukey HSD. Values not sharing the same letter indicate a significant difference (P <0.05). Bars represent means  $\pm$  one standard error.

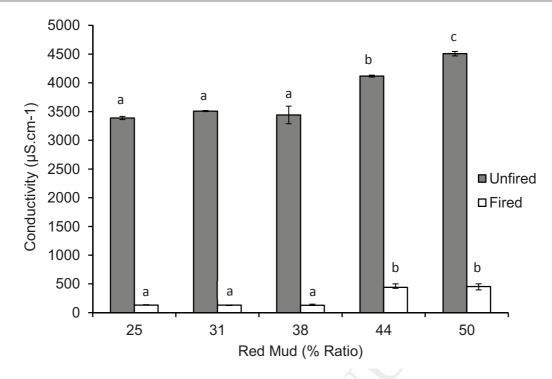
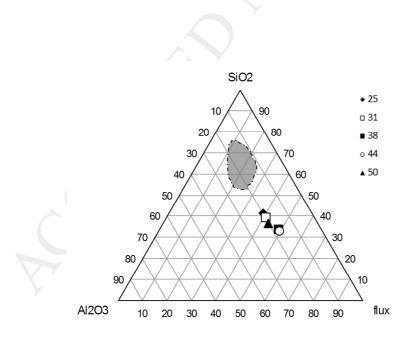


Figure 4. Conductivity of aggregates before and after sintering. Means analysed with ANOVA and differences separated with Tukey HSD. Values not sharing the same letter indicate a significant difference (P <0.05). Bars represent means  $\pm$  one standard error.



**Figure 5.** Riley's composition diagram showing the positions of the different ratios of red mud replacement pellets (unfired) and their relation to the ideal bloating area (shown in grey).

# Highlights

- We successfully manufactured lightweight aggregate using bauxite residue (red mud).
- 44 % red mud replacement most successful for strength and water holding capacity.
- 44 % also produced highest density due to insufficient glass phase viscosity,
- All ratios significantly reduced in pH after firing to around pH 8.
- Leachability of all aggregates below levels set by European landfill directive (2003/33/EC).