

# PRODUCTION OF CLAY COATED LIGHTWEIGHT FILL MATERIALS FROM AIR POLLUTION CONTROL RESIDUES (APCR)

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## Abstract

Air pollution control residues (APCr) from energy-from-waste are classified as hazardous due to their high heavy metal content and alkalinity. Recycling attempts using thermal treatment to produce a ceramic material known as lightweight aggregate have been successful in incorporating a maximum of 10% of APCr in the final product's structure. The aim of this work was to increase this incorporation by producing macro-encapsulated APCr granules with a clay coating. APCr has been washed with deionized water, milled and mixed with different concentrations of sodium silicate to form into granules. Sodium silicate solution was added to the mix to enhance the content of silicate and flux. The green pellets were coated with clay and sintered in a laboratory furnace at 1150 °C. The effect of addition of sodium silicate on particle density, water absorption and compressive strength has been discussed. Leaching behaviour of heavy metals and soluble anions from the sintered granule was examined according to BS EN 12457. Optical micrographs of the sintered products were investigated to reveal the microstructure of the binding interface between APCr and clay coating. The results showed that incorporation of up to 30% of APCr in the structure of sintered granules is possible. The proposed clay coating technique is simple and can reduce the leaching behaviour of hazardous waste.

# 1 INTRODUCTION

During the waste incineration process, the generated exhaust gases must undergo a treatment through which the contaminants within the gases are separated in a solid filtrate, known as air pollution control residues (APCr). They are classified as a hazardous waste due to high levels of soluble chlorides, sulphate salts and lead, and are usually disposed of in special landfills (Amutha Rani et al., 2008a). Approximately, 200,000 tonnes of APCr is produced in the UK annually, a number which is expected to increase due to the UK's growing incineration capacity (Astrup, 2008).

Current disposal, treatment and management options for APCr, alongside a number of alternative recycling technologies, are summarized in Table 1. APCr with the current compositions cannot meet the waste acceptance criteria set by the EU for hazardous landfills (Quina et al., 2008b). In addition, traditional treatments such as solidification with a binder have been associated with a significant increase in the volume of waste and long-term instability due to the high salt content of residues (Quina et al., 2008a). Carbonation has been shown to be only able to temporarily stabilize the material before final disposal (Zhang et al., 2008). Other chemical stabilization methods using caustic solutions such as soluble sodium silicate, ortho-phosphoric acid and sodium carbonate are reported to have a positive effect on leaching of Pb and Zn but still problematic in case of chlorides, implying the need for a washing stage (Quina et al., 2010, Shirley and Black, 2011).

**Table 8, Current options in the UK's to deal with APCr, taken from (Amutha Rani et al., 2008a).**

Disposal/treatment options	Treatment technologies	Thermal treatment
<ul style="list-style-type: none"> <li>• Disposal to hazardous waste landfill</li> <li>• Storage in deep salt mines</li> <li>• waste acid treatment</li> </ul>	<ul style="list-style-type: none"> <li>• washing</li> <li>• Chemical stabilisation processes</li> <li>• Solidification</li> </ul>	<ul style="list-style-type: none"> <li>• Vitrification</li> <li>• Melting</li> <li>• Sintering</li> </ul>

Thermal treatments such as vitrification, melting and sintering are employed for producing environmentally stable glass-ceramic products (Trujillo-vazquez et al., 2009, Roether et al., 2010). In thermal vitrification process, silica and alumina are added to APCr and the mix is melted under reducing conditions using DC plasma arc technology. This technique has been shown to be effective in encapsulating the volatile heavy metals and soluble salts into an amorphous matrix, and also in preventing the generation of NO<sub>x</sub> and HCl due to the presence of an inert argon atmosphere (Amutha Rani et al., 2008b). However, the main drawback of the plasma technology is the high cost that is required for the input power (Quina et al., 2008a). Studies on producing lightweight aggregate from APCr and clay have been successful to incorporate a maximum of 10% of washed APCr in the structure of products however, the technical advantage of this method is still in doubt (Quina et al., 2014a, Quina et al., 2014b). This work aimed at producing clay-coated APCr granules by using thermal treatment. The objective was to employ a combination of methods such as washing, chemical and physical stabilization and sintering to obtain optimal mechanical properties and minimal leaching of contaminant.

## 2 EXPERIMENTAL

### 2.1 Materials

APCr samples were collected from one the UK's energy from waste (EFW) plants. The clay was taken from an excavated clay recycling plant in East London. Sodium silicate solution (AVONCHEM, UK) with a module of approximately 3.2 was used as a sintering promoter. APCr were characterised for total metals, pH and alkaline reserve, total chloride and total dissolvable solids (TDS). APCr were washed with 10 times of distilled water (L/S=10) for 1 hour, vacuum filtered and dried at 105 °C until they reach a constant weight.

### 2.2 Manufacture of granules

A washed sample of APCr was milled in a planetary ball mill at 300 rpm to reach a maximum particle size of 125 µm. The milled sample was then mixed with sodium silicate at concentrations ranging from 20% to 50% with 10% increments and to form into wet 'green' granules (water was added in this stage to help the granulation). The 'green' granules were dipped in dried clay with particle size <125 µm in a rotational custom made drum granulator (diameter: 350 mm, rotational speed: 100 rpm). The batch was processed for 10 minutes to allow a clay-coating to be deposited on the wet surface of APCr/sodium silicate granules. The granules were checked during the process to control the coating thickness. When the coating reached 1±0.3 mm, the process was terminated. The coated granules with particle size ranging from 3mm to 6mm were dried at 105 °C for 2 hours and fired at 1150 °C for 20 minutes in a muffle furnace.

### 2.3 Characterization of sintered granules

Density, water absorption capacity and compressive strength of the sintered clay coated granules were evaluated as three main indications of final products' mechanical properties, using following formulas:

Particle density ( $\rho_{dr}$ ) (specific gravity) and water absorption (WA) were calculated according to BS EN 1097-6:2000 Where,  $M_1$  is the mass of the saturated surface-dried granules (24 h in water and dried in air);  $M_{im}$  is the apparent mass (immersed mass); and  $M_d$  is the mass of oven-dried granules.

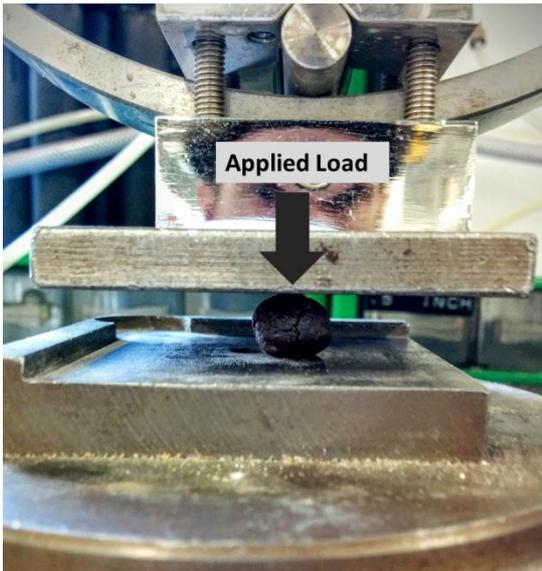
$$\rho_{dr} = (\rho_w \times M_d) / (M_{ssd} - M_{im})$$

$$WA = 100 \times (M_{ssd} - M_d) / M_d$$

Compressive strength was calculated by loading the granules to fracture between two parallel rigid surfaces and using the following equation (Cheeseman et al., 2005):

$$S = (2.8Pc) / (\pi X^2)$$

$Pc$  is the fracture load (N) and  $X$  is the distance (mm) between the loading points. A testing apparatus with a 4.55 kN capacity load-ring was used. Figure 1 shows the position of an individual granule under the load. The movement of the upper plate was adjusted at 0.5 mm/min.



**Figure 11. Position of a granule under the applied compressive load.**

For microstructural characterization, a Keyence corporation (Japan) VHX-2000 optical microscope with lenses VH-Z20R/W and VH-Z500R/W was used.

Leaching analysis was performed according the European standard EN 12457. For the test, the granules were leached in deionised water at a liquid to solid ratio (L/S) of 10 l/kg under constant rotation for 24 h. The test was carried out at the materials own pH. The resulted leachate was then filtered and the concentrations of inorganic constituents were measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES). The limit values established in European Landfill Directive (2003/33/EC) were used as a reference criteria to compare the measured concentrations (Rocca et al., 2012).

### 3 RESULTS AND DISCUSSIONS

#### 3.1 Characterization of APCr and clay

Properties of the APCr sample including pH, alkali reserve, total metals and chloride content together with the results of leaching test (BS EN 12457-2) and waste acceptance criteria (WAC) limits for hazardous landfills are shown in table 2. Among metals, leaching of lead was extremely high (723 mg/kg) which was expected due to its high total concentration (1,840 mg/kg) in as-received APCr sample. In addition, high levels of chloride, total dissolved solids (TDS) and dissolved organic carbon (DOC) exceeded the acceptance criteria for hazardous landfill.

**Table 9, Bulk chemical compositions of the APCr sample and the results of BS 12457-2 leaching test compared with limits for hazardous waste.**

Total metals mg/kg		BS 12457-2 LS = 10 (mg/kg)		Hazardous Limits as expressed in landfill directive mg/kg
As	<3.82	As	<1.46	25
Ba	429	Ba	126	300
Cd	116	Cd	<0.081	5
Cr	114	Cr	5.24	70
Cu	611	Cu	14.2	100
Pb	1,840	Hg	<0.353	2
Hg	<0.92	Mo	2.03	30
Mo	11	Ni	0.13	40
Ni	41	Pb	723	50
Sb	543	Sb	<1.383	5
Se	<1.67	Se	<0.664	7
Zn	9,190	Zn	168	20
pH	12.68	Cl	199000	25000
Alkali Reserve	20.96	F	37.7	500
Ca	303,000	SO4	13600	50000
K	39,300	TDS	353000	100000
Na	37,800	DOC	162	100
Cl	199,000			

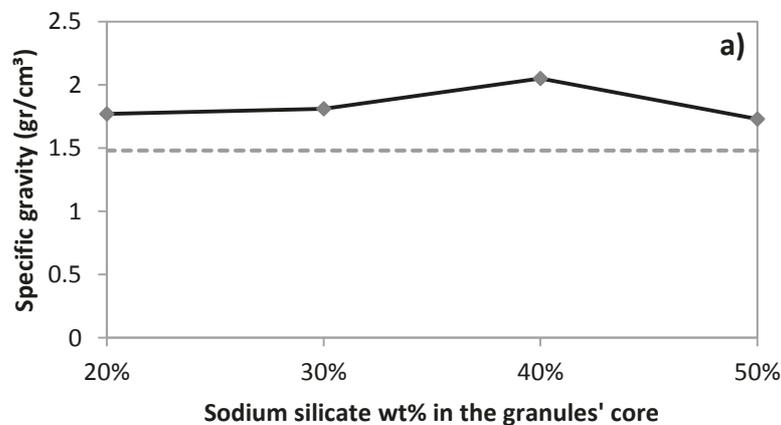
### 3.2 Sintered granules

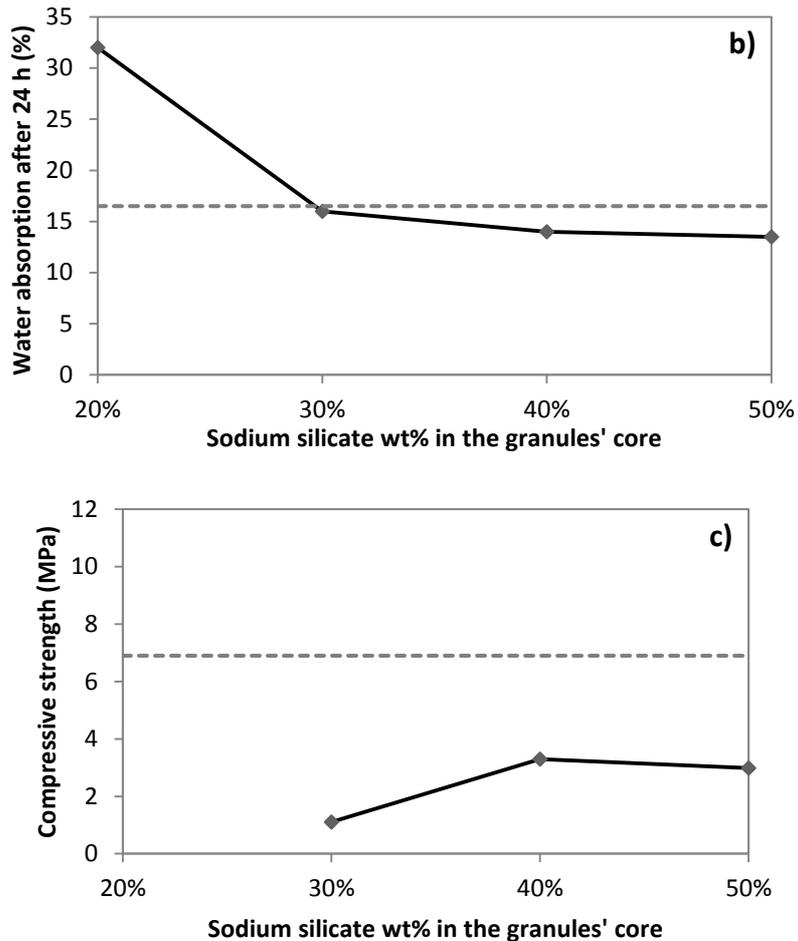
Figure 2a – 2d show granules with a sintered clay coating and a bright APCr core containing 20, 30, 40 and 50 wt% sodium silicate. The sintered granules with 20% sodium silicate were weak and chalky with a fractured coating. Coating fractures in Figure 2a and Figure 2b also suggest shrinkage in the coating during the firing process. Adding 40% of sodium silicate to the core could act as a sintering promoter and affect the clay particles to bind in a liquid phase. The optimum concentration of sodium silicate in the core was found to be 40% which could produce regular granules with minimal coating fractures. 50% addition of sodium silicate was detrimental as it caused agglomeration and excessive melting of both core and coating.



**Figure 2. Granules with a sintered clay coating and APCr core containing: a) 20%, b) 30%, c) 40% and d) 50% sodium silicate.**

Figure 3 shows the effect of sodium silicate addition on density (specific gravity), water absorption capacity and compressive strength of the sintered granules. The dashed line represents the mechanical properties of a commercially available lightweight aggregate called Lytag (Cheeseman et al., 2005). Sodium silicate addition up to 40% increased the mean density to 2 gr/cm<sup>3</sup>. Above that concentration the mean density decreased to 1.73 gr/cm<sup>3</sup>. Water absorption significantly decreased with sodium silicate addition and reached below the Lytag's capacity for granules with a core containing 30% sodium silicate. The highest compressive strength, 3.3 MPa, was achieved with 40% sodium silicate. The observed trends in water absorption and compressive strength with addition of sodium silicate, are possibly due to the fluxing effect of sodium silicate which would promote the liquid phase sintering and thus, improve the ceramic properties of both core and coating (Bourtsalas et al., 2015). The presence of liquid phase sintering was investigated by analysing the microstructure of the sintered granules with a core with 40% sodium silicate, using an optical microscope. For this batch of granules, the amount of incorporated APCr was estimated between 25 to 30%.



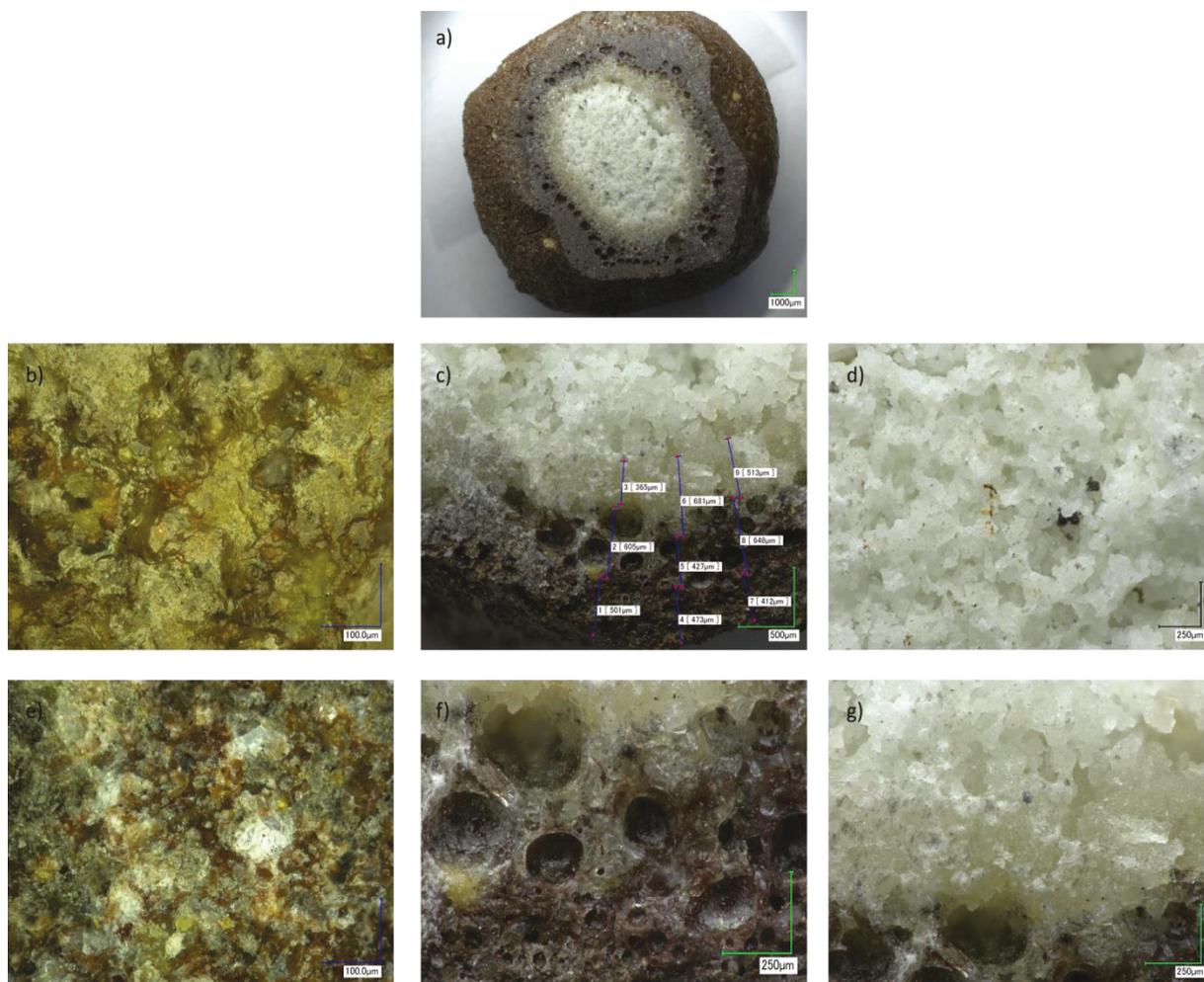


**Figure 3. Effect of addition of sodium silicate to the APCr mix on the mechanical properties of the sintered granules: a) specific gravity, b) water absorption after 24 hours, and c) compressive strength of individual pellets. The dashed line shows approximate values for Lytag.**

Figure 4 shows optical micrographs of the sintered granules structure with 40% sodium silicate. The clay coating was polished to access the APCr core (Figure 4a). This revealed a number of layers and microstructural features that had been generated during the firing process. Figure 4b shows an image of the clay coating surface. Presence of a vitrified glassy layer on the surface of the clay coating was detected in most areas. It must be noted that this glassy layer was non-porous and crack-free which could have affected the possible leaching of contaminants. Figure 4c shows three distinctive layers and their thicknesses measured at different spots. First, a sintered clay layer with a thickness between 400 $\mu$ m and 500 $\mu$ m measured at three spots numbered as 1, 4 and 7. Second, a bloated layer measured at 2, 5 and 8 composed of bubbles with various sizes. Third, an intermediate densified silicate based layer with a thickness up to 680 $\mu$ m measured at 3, 6 and 9.

Figure 4e – 4g show magnified images of each distinctive layer. A semi-crystalline structure for the clay coating can be seen in Figure 4e. In addition, the formation of a densified layer at the vicinity of clay (Figure 4g) was possibly due to the accumulation of silicates (dissolved in water). Dry clay particles as they attach to the wet surface of the APCr granules (during the coating process) may have absorbed the silicate solution towards the surface of the core and facilitate the formation of an adjacent silicate based layer. The bloating effect, shown in Figure 4f, can be explained through similar

reactions that happen during the production of lightweight aggregate (de' Gennaro et al., 2004). Here, the fluxing capability of the absorbed sodium silicate into clay, has resulted in phases with lower melting points which enveloped any released gaseous phase at that temperature (Riley, 1951).



**Figure 4. Optical micrographs of the sintered granules with 40% sodium silicate: a) polished granules revealing the core and the clay coating, b) vitriified and non-porous surface of the clay coating, c) thickness measurements of the layered structure, d) grains of APCr and sodium silicate with some inclusions, e) sintered semi-crystalline clay coating, f) bloating effect, and g) a densified silicate based intermediate layer.**

Table 3 shows the results of BS EN 12457-2 leaching test and limit values in the EU landfill directive for hazardous, non-hazardous and inert waste. Comparing with leaching test results of untreated APCr (shown in table 2) it is evident that the leachate's concentrations in all cases have decreased to a large extent. For example, leaching of Pb, Zn and Cl which had exceeded the limits for hazardous waste, reached below the limit values for inert waste after the thermal treatment. However, despite passing the criteria for hazardous and non-hazardous waste, the manufactured granules could not be classified as inert since levels of Cr, F, SO<sub>4</sub> and total dissolved solids were still slightly higher than the specified limit values. Leaching of these constituents could be originated both from the APCr internal structure (granule's core) and the clay coating which was in contact with the water for a long time during the leaching test. It is more likely that the contaminants have leached out through capillary pores within the coating. These pores may have remained in the structure of the coating as

a result of incomplete sintering or lack of surface verification. Here, it must be noted that the initial washing stage had already reduced the concentration of Cl in APCr and its low concentration in the leachate is mainly due to the fact that Cl compounds are very soluble and solubilise rapidly while other anions such as sulphate remain within the material during a short washing stage (Chimenos et al., 2005, Lampris et al., 2008). To solve the leaching problem, more control over the firing process and possibly use of a rotary kiln are suggested.

**Table 10, BS 12457-2 leaching test results and concentration limits (as expressed in the EU landfill directive 2003/33/EC) for landfill for hazardous, non-hazardous and inert waste.**

<b>Constituents</b>	<b>BS 12457-2 LS = 10 (mg/kg)</b>	<b>Hazardous Limits As expressed in landfill directive (mg/kg)</b>	<b>Non-Hazardous Limits As expressed in landfill directive (mg/kg)</b>	<b>Inert Limits As expressed in landfill directive (mg/kg)</b>
As	<1.460	25	2	0.5
Ba	1.4	300	100	20
Cd	<0.081	5	1	0.04
Cr	0.7	70	10	0.5
Cu	<0.356	100	50	2
Hg	<0.353	2	0.2	0.01
Mo	<0.819	30	10	0.5
Ni	<0.104	40	10	0.4
Pb	0.3	50	10	0.5
Sb	<1.383	5	0.7	0.06
Se	<0.664	7	0.5	0.1
Zn	<3.095	20	50	4
Cl	<51.0	25000	15000	800
F	<20.3	500	150	10
SO4	1994.4	50000	20000	1000
TDS	4300	100000	60000	4000
DOC	<300.00	100	800	500

## 4 CONCLUSION

This work proposed a simple and effective technique for recycling of APCr which is one of the most problematic hazardous waste. It was demonstrated that mixing APCr with sodium silicate for granulation and applying a clay coating through thermal treatment can result in a product with suitable mechanical properties which could incorporate up to 30% APCr in its structure. The addition of sodium silicate was beneficial in reducing the overall sintering temperature and promoted the liquid phase sintering which improved the strength of the granules. Optical micrographs revealed the presence of three distinctive layers in the structure of granules including: a sintered clay based coating outer layer, a bloated intermediate layer and a densified silicate rich surrounding the internal core. Leaching of the contaminants was significantly decreased below the EU limit values for hazardous and non-hazardous waste. The study showed that a clay coating may have the potential for recycling APCr into an inert fill material that can be utilised for civil engineering applications.

## REFERENCES

- Amutha Rani, D., Boccaccini, A. R., Deegan, D. and Cheeseman, C. R. (2008a) 'Air pollution control residues from waste incineration: Current UK situation and assessment of alternative technologies', *Waste Management*, 28(11), pp. 2279-2292.
- Amutha Rani, D., Gomez, E., Boccaccini, A. R., Hao, L., Deegan, D. and Cheeseman, C. R. (2008b) 'Plasma treatment of air pollution control residues', *Waste Management*, 28(7), pp. 1254-1262.
- Astrup, T. (2008) 'Management of APC residues from WtE plants. An overview of management options and treatment methods'.
- Bourtsalas, A., Vandeperre, L. J., Grimes, S. M., Themelis, N. and Cheeseman, C. R. (2015) 'Production of pyroxene ceramics from the fine fraction of incinerator bottom ash', *Waste Management*, 45, pp. 217-225.
- Cheeseman, C. R., Makinde, A. and Bethanis, S. (2005) 'Properties of lightweight aggregate produced by rapid sintering of incinerator bottom ash', *Resources, Conservation and Recycling*, 43(2), pp. 147-162.
- Chimenos, J. M., Fernández, A. I., Cervantes, A., Miralles, L., Fernández, M. A. and Espiell, F. (2005) 'Optimizing the APC residue washing process to minimize the release of chloride and heavy metals', *Waste Management*, 25(7), pp. 686-693.
- de' Gennaro, R., Cappelletti, P., Cerri, G., de' Gennaro, M., Dondi, M. and Langella, A. (2004) 'Zeolitic tuffs as raw materials for lightweight aggregates', *Applied Clay Science*, 25(1-2), pp. 71-81.
- Lampris, C., Stegemann, J. A. and Cheeseman, C. R. (2008) 'Chloride leaching from air pollution control residues solidified using ground granulated blast furnace slag', *Chemosphere*, 73(9), pp. 1544-1549.

- Quina, M. J., Almeida, M. A., Santos, R., Bordado, J. M. and Quinta-Ferreira, R. M. (2014a) 'Compatibility analysis of municipal solid waste incineration residues and clay for producing lightweight aggregates', *Applied Clay Science*, 102(0), pp. 71-80.
- Quina, M. J., Bordado, J. C. and Quinta-Ferreira, R. M. (2008a) 'Treatment and use of air pollution control residues from MSW incineration: An overview', *Waste Management*, 28(11), pp. 2097-2121.
- Quina, M. J., Bordado, J. C. M. and Quinta-Ferreira, R. M. (2010) 'Chemical stabilization of air pollution control residues from municipal solid waste incineration', *Journal of Hazardous Materials*, 179(1-3), pp. 382-392.
- Quina, M. J., Bordado, J. M. and Quinta-Ferreira, R. M. (2014b) 'Recycling of air pollution control residues from municipal solid waste incineration into lightweight aggregates', *Waste Management*, 34(2), pp. 430-438.
- Quina, M. J., Santos, R. C., Bordado, J. C. and Quinta-Ferreira, R. M. (2008b) 'Characterization of air pollution control residues produced in a municipal solid waste incinerator in Portugal', *Journal of Hazardous Materials*, 152(2), pp. 853-869.
- Riley, C. M. (1951) 'Relation of Chemical Properties to the Bloating of Clays', *Journal of the American Ceramic Society*, 34(4), pp. 121-128.
- Rocca, S., van Zomeren, A., Costa, G., Dijkstra, J. J., Comans, R. N. J. and Lombardi, F. (2012) 'Characterisation of major component leaching and buffering capacity of RDF incineration and gasification bottom ash in relation to reuse or disposal scenarios', *Waste Management*, 32(4), pp. 759-768.
- Roether, J. A., Daniel, D. J., Amutha Rani, D., Deegan, D. E., Cheeseman, C. R. and Boccaccini, A. R. (2010) 'Properties of sintered glass-ceramics prepared from plasma vitrified air pollution control residues', *Journal of Hazardous Materials*, 173(1-3), pp. 563-569.
- Shirley, R. and Black, L. (2011) 'Alkali activated solidification/stabilisation of air pollution control residues and co-fired pulverised fuel ash', *Journal of Hazardous Materials*, 194, pp. 232-242.
- Trujillo-vazquez, A., Metiver-pignon, H., Tiruta-barna, L. and Piantone, P. (2009) 'Characterization of a mineral waste resulting from the melting treatment of air pollution control residues', *Waste Management*, 29(2), pp. 530-538.
- Zhang, H., He, P.-J., Shao, L.-M. and Lee, D.-J. (2008) 'Temporary stabilization of air pollution control residues using carbonation', *Waste Management*, 28(3), pp. 509-517.