

Stabilization of air pollution control residues by utilizing geopolymerisation to produce secondary building materials

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ABSTRACT

Incineration is a powerful waste management tool which is employed in many countries. However, air pollution control residues are a by-product produced as a result of flue gas treatment, a key requirement for incineration. Air pollution control residues are classified as hazardous waste and are becoming increasingly difficult to dispose of in the UK due to tightening legislation. Therefore recycling of air pollution control residues as secondary building materials is an attractive option. Geopolymerisation offers advantages with regards to stabilizing heavy metals and has been investigated here as a means to reducing leaching rates of key elements in air pollution control residues collected from three UK based incinerators. The role of soluble chloride phases was also investigated by pre-treating the air pollution control residues with a washing procedure. Geopolymerisation was found to immobilize metals such as Ba, Pb and Ni, however it did not positively affect the mobility of As, Sb and Se. Chloride leaching rates were also reduced although not to an acceptable level and the mobility of soluble chloride phases are one of the key challenges when attempting to reuse air pollution control residues.

1. INTRODUCTION

Management of municipal solid waste is a key challenge for urbanized nations globally and will intensify during the 21st century due to population growth, population density increase and limited land space for landfill sites. In the UK environmental concern relating to the use of landfill as a management option for waste has resulted in incineration seeing growth as an alternative disposal route.

However, when municipal solid waste is incinerated two by-product waste streams are generated, bottom ash and air pollution control (APC) residues. APC residues are produced as a result of flue gas treatment by scrubbing of acid gases, generally by injection of a calcium-based reagent. The flue gas is also treated to remove other hazardous components such as mercury, NO_x, and toxic organic compounds such as dioxins and furans. The gas then passes through a filter, where the particulates in the flue gas are removed as APC residues. The resulting APC residues are classified as absolute hazardous waste (19 01 07*) under the European Waste Catalogue. As a result APC residues are often disposed of at hazardous landfill sites, however in some cases methods such as stabilization/solidification by addition of cement or waste acid to create a product are employed and the subsequent product is disposed of at non-

hazardous landfill sites (Rani *et al.* 2008, Quina *et al.* 2008).

The APC residue waste stream is increasing in volume each year. As of 2014, the UK had around 47 dedicated incinerators with a capacity of ~21 tonnes per annum. APC residues generally account for around 2-5% by weight of the original waste incinerated resulting in several hundred thousand tonnes produced per annum currently. New facilities which have been granted planning permission account for ~14 tonnes per annum of waste incineration capacity which would result in a significant increase in the volume of APC residues produced.

In the UK, APC residues are currently disposed of in landfill sites under derogations to leaching limits which are currently under review and may potentially be removed. Landfill sites test waste received prior to disposal and must comply with Waste Acceptance Criteria (WAC), which include a number of leaching limits for metals, sulphates and chlorides. However, when considering APC residues, the WAC limits are increased by three times (referred to as WAC derogations) due to the troublesome nature of the waste stream, which allows APC residues to be directly disposed of at hazardous landfill sites. In a 2010 report DEFRA stated that the WAC derogations were to end. The removal of the derogations would increase demand on the facilities treating APC residues presently. The

significant impact of removing the derogations led the Environment Agency to seek consultation from within the industry (Environment Agency, 2014).

It is therefore clear that the APC residue waste stream requires urgent attention with regard to treatment or re-use. One option for re-use is in secondary building materials and in recent years several UK based companies have produced aggregates from APC residues. One treatment option that has been recently explored is geopolymerisation as a means to immobilize heavy metals in APC residues (Lancellotti. *et al.* 2010, Luna Galiano *et al.* 2011). Geopolymerisation offers a matrix in which a range of metallic elements can be immobilized (Provis and Van Deventer, 2009). However, the soluble chloride species that exist in APC residues in high concentrations pose a potential problem as their mobility can alter the pore structure of the geopolymer resulting in physical degradation and reducing the immobilization effect (Zheng *et al.* 2011).

Previous research (e.g De Boom and Degrez, 2012) has highlighted distinctions between various types of 'fly ash' and APC residues. The technology employed during flue gas treatment plays an important role in defining the characteristics of APC residues and therefore such factors must be considered when recommending treatment methods for the waste stream. This work aims to investigate the effect of geopolymerisation on the immobilization of heavy metals whilst using previous insights to enhance interpretation. The role of problematic soluble chloride phases is also investigated through washing tests.

2. MATERIALS AND METHODS

APC residues were collected from three UK based incinerators which represent different burn conditions, operating capacities, ages and scrubber types. These factors have implications on the characteristics of the APC residues (Alba *et al.* 1997, De Boom and Degrez, 2012) which were studied previously (Mustard *et al.* 2015). The incinerators are referred to as I1-I3 and the corresponding APC residue samples referred to as S1-S3. APC residue samples were collected at the start of this research project, 2014, and were stored in air tight containers. Sub-samples were obtained by riffle splitting. The morphology of the APCr was evaluated using a JEOL 6480LV SEM at 15 kV. The JEOL 6480LV was equipped with an Oxford INCA X-Act SDD X-ray detector for EDX analysis which was operated under low vacuum at 15 kV and a large number of spot samples were collected.

S1-S3 were washed using a method described by Zhu *et al.* (2008) which was demonstrated to effectively remove soluble chlorides from similar residues. The wash was a double-stage procedure; the first wash was performed at a (liquid)/(solid)s

ratio of 3/1 for 5 minutes. The sample was then filtered to collect the APC residue and then washed a second time at a l/s ratio of 10/1 for 30 minutes. The resulting sample was then filtered and placed in a 105°C oven until the mass was stable. The dried sample was then ground into a fine powder and sub-samples analysed. X-ray diffraction was performed using a Bruker AXS D8 Advance with Vantec-1 Detector operated at 40kV, 40mA. The radiation source was CuK α ($\lambda = 1.5418 \text{ \AA}$), the step size 0.02° and the range 5 to 80° 2 θ .

200g of raw (APC residue samples as collected from I1-I3) S1-S3 and washed S1-S3 which was mixed with 100g metakaolin and a 6.5 molar NaOH solution was used as an alkaline activator. Additional water was then added to achieve roughly the same workability prior to casting. Samples were then vibrated for 90s on a vibrating table to remove air bubbles and all samples were placed in a 55°C oven for 24h.

Leaching tests were designed to be at least in accordance with BS EN 12457-2:2002, used by the Environment Agency for WAC determination, with several key differences. First, the extraction was performed at a l/s ratio of 10/1 over a 24 hour period, however the agitation mechanism used was a magnetic stirrer. Secondly, and of most significance, the samples were finely ground, in direct contradiction to the standard. As the raw APC residues have a particle size ranging from 0.1-600 μm with most particles occurring in the 2-30 μm size range. The APC residues geopolymer samples had a diameter of ~100mm and a depth of ~40mm. According to the standard leaching test these samples are to be crushed to a particle size of less than 4mm, however the resulting particle size distribution of the test sample would greatly exceed the average particle size of the raw APC residues. The result may be exaggerating the physical encapsulation effect of the geopolymerisation, as well as surface area interactions. Eluate was then passed through a 0.45 μm filter prior to analysis at a commercial laboratory by ICP-MS to determine metals and Kone to determine anions. In some cases samples were omitted from analysis, due to a lack of test material.

3. RESULTS AND DISCUSSION

XRD analysis identified (Figure 1): Anhydrite (CaSO₄), Calcite (CaCO₃), Halite (NaCl), Portlandite (Ca(OH)₂), Quartz (SiO₂) and Sylvite (KCl) in the unwashed APC residue samples. S3 did not contain Portlandite, unlike S1 and S2. This is a result of the high efficiency of I3 which means that a vast majority of the lime injected into the flue gas is consumed by reactions, leaving little residual lime in S3. S1 on the other hand contains a more substantial Quartz peak in comparison to S2 and S3, which is a result of boiler ash being incorporated

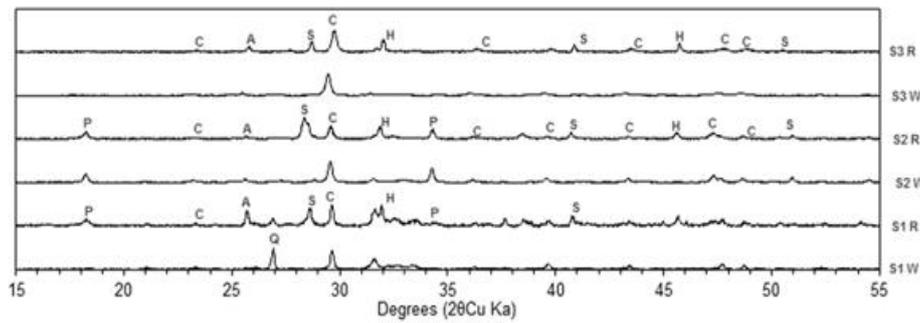


Figure 1. XRD diffraction pattern of washed (W) and unwashed APC residues (R). A- Anhydrite, C- Calcite, H- Halite, P- Portlandite, Q- Quartz, S- Sylvite.

into the APC residue – a practice at I1, which is atypical. The washed residues do not contain the strong chloride phase peaks in comparison to the unwashed residues, demonstrating that the main soluble phases are Halite and Sylvite. Washed S1 no longer contains the Portlandite peaks suggesting that carbonation has taken place. As S2 contains Portlandite peaks following the washing procedure it is possible to infer with previous data (Mustard *et al.* 2015) that there is a higher quantity of lime, likely a result of the lower efficiency of I2, the opposite effect as described previously about I3.

Leaching rates for most metals analysed were in accordance with inert landfill WAC (Table 1), which is used here as a point of comparison for leaching rates comparable to those that may be suitable for use as secondary building materials. Cl leaching rates are particularly high and the washing procedure removed a significant proportion of the soluble Cl phases and therefore the washed geopolymer samples show low leaching rates. In the unwashed geopolymer samples Cl leaching rates were reduced, although the extent accounted for by physical encapsulation and dilution is not quantifiable from these results.

It is probable that physical encapsulation played a minimal role due to the nature of the leaching test, and that a dilution effect alone would not explain the reduction. Geopolymerisation, acting to immobilize a fraction of the Cl, accounts to some extent for the reduction in Cl leaching rates observed.

Metals immobilisation in the geopolymer samples is more complex. Some metals, such as Pb, Ba and Ni, were immobilised in the geopolymer samples, whereas others, such as As, Cr and Se, were observed to have higher leaching rates. Zn showed no trend and an anomalous result was observed where leaching (Washed APC Geopolymer S2) was dramatically increased relative to S2 APC residue.

Previous authors (Quina *et al.* 2008) have suggested that relative components of APC residues vary both between incinerators and over time. SEM-EDX analysis of S1-S3 (Figure 2 and 3) provides insight into the distribution of metals in

Table 1. Composition of eluate from APC residues and resulting geopolymer samples. Values in light italics exceed WAC limits for inert landfill sites.

EN 12457-2 (mg/kg)	Washed APC Geopolymer		Raw APC Geopolymer			APC residues	
	S1	S2	S1	S2	S3	S2	S3
	As	0.50	<i>0.56</i>	0.07	0.19	0.06	0.137
Ba	0.02	0.01	0.04	0.06	0.30	9.340	5.460
Cd	0.00	0.00	0.00	0.00	0.00	0.001	0.001
Cr	0.18	<i>0.84</i>	0.15	0.24	0.04	0.229	0.052
Cu	0.01	0.06	0.00	0.05	0.00	0.098	0.013
Mo	0.35	0.30	0.26	0.26	0.17	0.195	0.108
Ni	0.00	0.00	0.00	0.00	0.01	0.095	0.091
Pb	0.10	0.14	0.19	0.18	0.28	<i>5.530</i>	<i>1.210</i>
Sb	<i>0.34</i>	<i>0.81</i>	<i>0.17</i>	<i>0.64</i>	0.01	<i>0.553</i>	<i>0.516</i>
Se	<i>0.16</i>	<i>0.34</i>	<i>0.16</i>	<i>0.28</i>	<i>0.22</i>	0.003	0.006
Zn	1.82	<i>15.50</i>	1.65	3.52	1.12	<i>4.090</i>	0.768
Cl	276	549	<i>4100</i>	<i>6720</i>	<i>8410</i>	<i>17400</i>	<i>18200</i>
SO₄	1780	<i>2770</i>	<i>1550</i>	<i>2110</i>	<i>2370</i>	893	<i>2130</i>

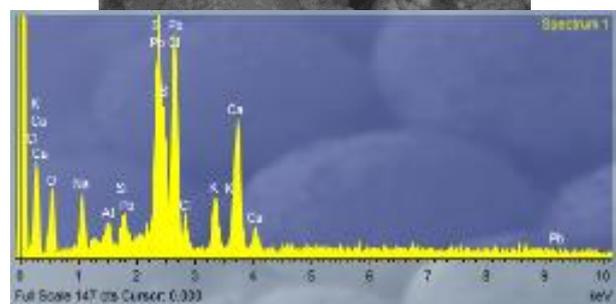
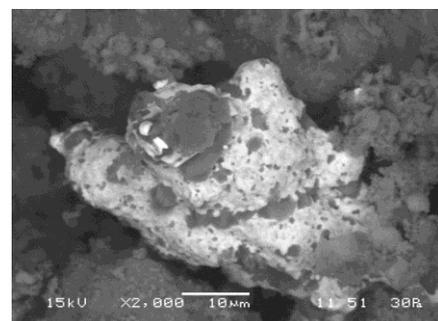


Figure 2. SEM image of S2 APC residue and corresponding EDX data.

APC residues. S1 and S2 were observed to have concentrated clusters of metals such as Zn, Pb, Ba and Fe. The metals appear to be crystalline in structure in some cases, and in others are condensed onto the surface of particles, such as that shown in Figure 2, Pb coating the surface of a particle primarily consisting of Ca and Cl. As such crystalline metal phases are likely to be a very small

fraction of the APC residue sample, therefore are likely below the detection limit of the XRD analysis.

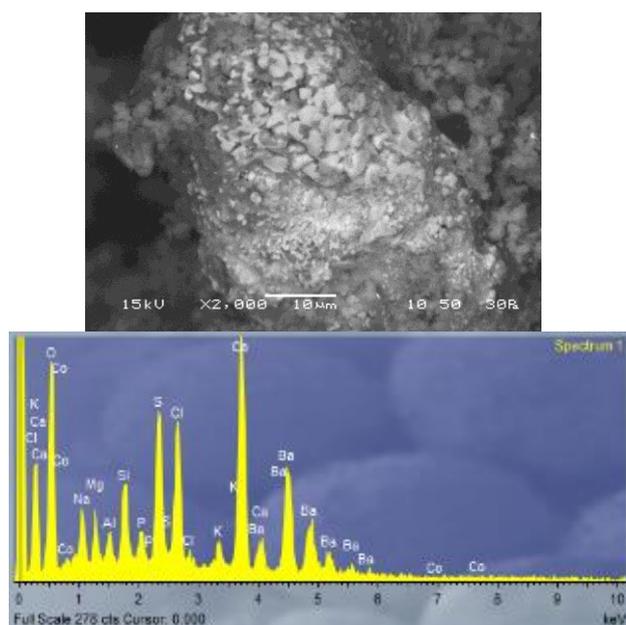


Figure 3. SEM image of S1 APC residue and corresponding EDX data.

S3 metals appeared to be more heterogeneously distributed, relative to S1 and S2. This characteristic of S3 may be due to the operating conditions at I3 – a highly modern plant where burn conditions and air pollution control is more efficient than at I1 and I2. These findings may explain the anomalous data point for Zn, the homogenous distribution of metals in S2 may result in measurable differences between subsamples. The implication of this finding is that older incineration plants may produce APC residues that are significantly more variable in metals concentrations both over time and between subsamples of a spot sample, relative to more modern facilities.

3. Conclusions

Geopolymerisation was observed to offer beneficial immobilisation effects on some metals in APC residues, such as Ba, Pb and Ni, however leaching rates of other metals such as As, Sb and Se were unaffected. Washing the APC residues did not have a clear impact on metals immobilisation rates, although the removal of soluble species may have indirect effects such as improved physical structure of resulting samples, increasing encapsulation effects. APC residues that are more heterogeneous in nature, such as those from older incineration facilities, may require specific attention due to highly variable metals concentrations between samples.

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