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Element composition and mineralogical characterisation of air pollution control residue from UK energy-from-waste facilities

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ABSTRACT

Air pollution control (APC) residues from energy-from-waste (EfW) are alkaline (corrosive) and contain high concentrations of metals, such as zinc and lead, and soluble salts, such as chlorides and sulphates. The EPA 3050B-extractable concentrations of 66 elements, including critical elements of strategic importance for advanced electronics and energy technologies, were determined in eight APC residues from six UK EfW facilities. The concentrations of Ag (6–15 mg/kg) and In (1–13 mg/kg), as well as potential pollutants, especially Zn (0.26–0.73 wt.%), Pb (0.05–0.2 wt.%), As, Cd, Cu, Mo, Sb, Sn and Se were found to be enriched in all APC residues compared to average crustal abundances. Results from a combination of scanning electron microscopy with energy dispersive X-ray spectroscopy and also powder X-ray diffraction, thermal analysis and Fourier transform infrared spectroscopy give an exceptionally full understanding of the mineralogy of these residues, which is discussed in the context of other results in the literature. The present work has shown that the bulk of the crystalline phases present in the investigated APC residues include Ca-based phases, such as $CaCl_xOH_{2-x}$, $CaCO_3$, $Ca(OH)_2$, $CaSO_4$, and CaO, as well as soluble salts, such as NaCl and KCl. Poorly-crystalline aragonite was identified by FTIR. Sulphur appears to have complex redox speciation, presenting as both anhydrite and hannebachite in some UK EfW APC residues. Hazardous elements (Zn and Pb) were widely associated with soluble Ca- and Cl-bearing phases (e.g. $CaCl_xOH_{2-x}$ and sylvite), as well as unburnt organic matter and aluminosilicates. Specific metal-bearing minerals were also detected in some samples: e.g., Pb present as cerussite; Zn in gahnite, zincowoodwardite and copper nickel zinc oxide; Cu in tenorite, copper nickel zinc oxide and fedotovite. Aluminium foil pieces were present and abundantly covered by fine phases, particularly in any cracks, probably in the form of Friedel's salt.

1. Introduction

1.1. Background

Air pollution control (APC) residues from energy-from-waste (EfW) represent only 2–6% of the original volume of the municipal solid waste (MSW). However, APC residues are classified as hazardous wastes because they are alkaline (corrosive) and contain high concentrations of metals (e.g., Pb, Zn, Cd, Cr, Cu, Hg), soluble salts, such as chlorides and sulphates, and toxic organic pollutants (e.g., dioxins and furans) due to volatilisation and condensation processes in the boiler and flue gas cleaning systems (Amutha Rani et al., 2008; Astrup et al., 2005, 2006; BREF, 2006; Chandler et al., 1997; De Boom and Degrez, 2012; Quina et al., 2008b, 2011). They are classified as hazardous wastes under code 19 01 07* in the European Waste Catalogue (EWC, European Commission Decision 2000/532/EC, 2000).

The work described in this paper was undertaken to gain a better understanding of the composition, mineralogy and nature of the host phases which can be responsible for leaching behaviour of potentially dangerous elements in APC residues from UK EfW facilities. A thorough analysis of these aspects is necessary to enable development of the best options to manage this waste. Novel findings from this work with multiple complex methods are discussed in the context of the literature in this area from the past two decades.

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1.2. Formation of APC residues

Flue gases from combustion processes contain fine particles that are entrained as the gas rises through the combustion chamber, known as fly ash, as well as acid gases (hydrogen chloride and sulphur dioxide) and trace quantities of uncombusted or uncombustible volatilised pollutants. APC residues are generated in the flue gas cleaning process. Although various APC schemes exist, commonly flue gases are cooled through heat exchange with water in a boiler and pass to a semi-dry scrubbing system, where acid gases are neutralized by the addition of hydrated lime ($Ca(OH)_2$). An ammonia scrubber may be used for reduction of nitrogen oxides (NOx) and sodium sulphide may be added to remove Hg; alternatively Hg may be removed with activated carbon, together with trace organic pollutants such as dioxins. Scrubbing residues and fly ash particles are then captured together by a fabric filter, producing APC residue (BREF, 2006; Chandler et al., 1997; Quina et al., 2011). In addition to chloride and sulphate captured in flue gas neutralisation, metals are concentrated in APC residues due to volatilisation and condensation processes in the boiler and flue gas cleaning systems (Astrup et al., 2006; Chandler et al., 1997; Song et al., 2004).

The boiling points of different phases (oxides, chlorides, sulphides, etc.) are primary factors which determine the presence of metals in APC residues (Davison et al., 1974; Fernandez et al., 1992). Klein et al. (1975) proposed the following classification of elements in relation to their accumulation (or not) in fly ash, according to their boiling points:

- Class I (e.g., Al, Ba, Ca, Co, Fe, K, Mg, Mn, Si, Sr, and Ti) elements have high boiling points, are not volatilised in the combustion area, but can be entrained as small particles or droplets that form the basis of the fly ash;
- Class II (e.g., As, Cd, Cu, Ga, Pb, Sb, Zn, and Se) elements are volatilised during combustion with subsequent condensation on the surface of the fly ash particles;
- Class III (e.g., Hg, Cl, and Br) elements volatilise and remain in the gas phase throughout the combustion process, but are removed by APC systems;
- Other elements (e.g., Cr, Cs, Na, Ni, U, and V) have mixed behaviour between Classes I and II.

In early work on this subject, Greenberg et al. (1978) assumed formation of chlorides of Pb, Sb, Cd, As, Zn, and Ni, whose boiling points are below 1273 K, in the combustion gas stream. Fernandez et al. (1992) investigated this vital issue in detail and concluded that three different relative stabilities are possible for metal compounds present in the incineration process, depending on the thermodynamic stability of their oxides and chlorides:

(1) If the oxide is more stable than the chloride, an element is transported mechanically and is found in the matrix of the fly ash particles;
(2) Elements whose oxides and chlorides have similar stabilities are transported by both volatilisation-condensation and mechanical mechanisms;
(3) If the chloride is more stable than the oxide, then the metal chloride volatilises and condenses on the surface of the fly ash particles, forming compounds with high solubility.

Fernandez et al. (1992) also showed that the formation-volatilisation-condensation of chlorides plays an important role in the transport of metals by the combustion gas stream. Verhulst et al. (1996) provided more information about elements under the conditions in MSW incinerators based on thermodynamic equilibrium calculations. For example, as temperature increases, solid $ZnCl_2$ converts to solid ZnO at around 280 °C, while $ZnCl_2$ vapour forms concurrently from about 140 °C. $ZnCl_2$ volatilisation increases with temperature, chloride concentration and reducing conditions, reaching about 70% at 800 °C if sufficient chloride is present. By contrast, the boiling point of $FeCl_3$ is approximately 650 °C, but the iron oxides are very stable and no significant amount of Fe is volatilised, even at 1100 °C. These authors also provided information about other elements (Hg, Cd, Pb, Cu, As, Sb, Mn, Mg, Al, Ti, and Sn). Recent work by Zhang et al. (2012) indicates that waste moisture content also influences element speciation. Thus, the presence of elements in specific species and their concentrations in fly ashes and APC residues definitely depends on the type of waste combusted, and its content of chlorine, sulphur and water; the oxidation level (amount of oxygen/(C + H)); temperature, and processing time, as well as boiling points of the different phases.

1.3. Mineralogical characterisation of APC residues

EfW APC residues are complex mixtures of various minerals, some originating from the entrained fly ash, and others imparted by the condensation and other reactions, as well as unreacted reagents, during flue gas cleaning. The morphology and mineralogy of APC residues has been investigated by several researchers (Alba et al., 1997; Bodenan and Deniard, 2003; Chandler et al., 1997; Dimech et al., 2008; Eighmy et al., 1995; Geysen et al., 2004; He et al., 2004; Le Forestier and Libourel, 1998; Li et al., 2004; Stuart and Kosson, 1994; Sun et al., 2008). APC residues may be composed of five types of particles, e.g., fused spheres, crystalline, polycrystalline, opaque and char (Chandler et al., 1997). As was mentioned by Le Forestier and Libourel (1998), APC residue contains unaltered entrained fly ash, reaction products (salts) and surplus reagent (lime). They also indicated that there are a wide range of particle shapes in APC residues, e.g., spheres, flakes, prisms, needles and sintered agglomerations of dust. Aluminosilicates produced from melt droplets during incineration of the municipal solid waste form smooth particles (Bayuseno and Schmahl, 2011; Eighmy et al., 1995; Kirby and Rimstidt, 1993). Char and agglomerated spheres were observed by Stuart and Kosson (1994) in lime spray drier scrubber residues from MSW incineration. The mineral phases previously identified in APC residues by instrumental methods are summarised in Table 1.

2. Materials

Eight APC residue samples were provided from six different UK EfW facilities, which burn predominantly MSW (European Waste Catalogue code 20 03 01) and its fractions, and range in capacity from less than a hundred thousand tonnes per year to several hundred thousand tonnes per year. The facilities are all mass-burn incinerators, with a minimum operating temperature of 850 °C, ammonia or urea injection for NOx abatement, lime injection to remove acid gases, activated carbon addition for sorption of metals and organic compounds, and capture of the APC residue by a fabric filter. The amount of APC residue collected ranged from 2.2–3.2% of the feed. The samples were provided on an anonymous basis and are identified here as A3, A8, A10, 1, 2, 4, 5, and 9. Samples A3, A8 and A10 were obtained from the same facility at different times. The samples were all “dusty” fine-grained powders, with the exception of A10, which had a fine sandy texture. The colour of these samples ranged from white to dark grey. Dark particles observed in the APC residues are likely to be unburnt carbon, whereas white particles are likely to be unreacted hydrated lime particles, injected for acid gas neutralisation. The APC residue moisture content was quite low and varied from 0.42–2.48% wet