THE ROLE OF COAL COMBUSTION PRODUCTS IN MANAGING THE BIOAVAILABILITY OF NUTRIENTS AND HEAVY METALS IN SOILS

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ABSTRACT

Coal provides the primary source of energy for many countries including Asia, South America, North America and Europe, and large quantities of waste products are produced during the combustion of coal in coal-fired power stations. This review paper gives an overview of the various types of coal combustion products (CCPs) and their utilization in various sectors, with a particular emphasis on the role of CCPs in managing the bioavailability of nutrients and heavy metals in relation to enhancing soil chemical fertility and mitigating metal contaminated soils. Currently, CCPs are used extensively in agricultural and construction industries. In agricultural industries, they are used primarily as an amendment to improve the physical and chemical properties of soil, as a source of liming material to ameliorate soil acidity and as a nutrient source to supply calcium and sulphur. In the construction industry, they are used mainly as a source of concrete, roofing material and road surface sealing. Increasingly, CCPs are used in the remediation of contaminated environments including control of acid mine drainage, mitigating phosphorus leaching in farm lands and immobilization of toxic metals in mine sites and agricultural soils.

Keywords: Coal, heavy metals, combustion products.

INTRODUCTION

Coal Combustion Products (CCPs) result from the combustion of coal, both in the presence and absence of bedding materials in coal-fired power stations. The volume of waste generated and problems with safe disposal make these by-products a menace to public health and environment. The rate of CCPs generation has been steadily increasing and is also predicted to ascend in the next two decades, mainly due to the intensification in coal usage for energy production (WEC, 2007). The rising Asian economies and the already developed nations like USA and Australia are projected to increase their energy needs thereby conflicting with Kyoto Protocol, although they are not part of the treaty.

Coal is derived from peat and as geological processes apply pressure to peat over time, it is transformed into the following types based on their organic maturity (WCI, 2009):

- *Lignite (brown coal)* - is the lowest rank of coal and used solely as fuel for steam-electric power generation.

- *Sub-bituminous coal* - properties range from those of lignite to bituminous coal and are used primarily as fuel for steam-electric power generation.

- *Bituminous coal* - a dense coal, usually black, sometimes dark brown, used primarily as fuel in steam-electric power generation, with substantial quantities also used for heat and power applications in manufacturing and to make coke.

- *Anthracite* - the highest rank of coal and is a harder, glossy and black coal used primarily for residential and commercial space heating.

Coal-fired power stations generate a number of by-products during the combustion of coal. Coal is usually burnt in a pulverised fuel furnace, resulting in two major types of ash products (CCPs) – the fly ash (FA) and the bottom ash (BA). The FA, which is recovered from the flue gas, has fine texture and is the major portion (90%) of ash produced. The remainder is collected at the bottom of the furnace as BA (coarser than FA). Apart from these two ash products, two other by-products - fluidised bed combustion (FBC) ash and flue gas de-sulphurisation (FGD) ash are produced as part of Clean Coal technologies, mainly to trap sulphur oxides (SO_x) produced during the combustion of high sulphur (S) containing coal (Stout *et al.,* 1998).

The use of CCPs as a soil amendment has been an ongoing area of investigation in many countries that produce coal and also use coal as an energy source. Following a brief overview of the types of CCPs, volume of production and their industrial, agricultural and environmental applications, the review focuses on the role of CCPs in managing the bioavailability of nutrients such as nitrogen, phosphorus, sulphur and calcium, and heavy metals such as cadmium, lead and mercury in relation to enhancing soil chemical fertility and mitigating metal contaminated soils.

Coal reserves are available in almost every country worldwide, with recoverable reserves in around 70 countries. At current production levels, proven coal reserves are estimated to last 122 years. In contrast, proven oil and gas reserves are equivalent to around 42 and 60 years at current production levels, respectively. This forecasts the potential continuing dominance of coal in energy production in the most successful industrial nations like United States, China, India, Australia and South Africa, where the coal power plants contribute over 50% to the energy needs of these countries (Figure 1) (WCI, 2008).

Global coal consumption is expected to increase at an average rate of 1.7% per year until 2020 and share of coal in world primary energy demand will remain stable at about 25% until 2020 (IEA, 2003). Although the coal industry welcomed the progress made in the Copenhagen summit (2009), it urged the governments to be more ambitious on climate change and work quickly to reach a legally binding agreement to replace the Kyoto Protocol as early as possible in 2010 (WCI, 2009). This will eventually drive the industrially powerful countries to invest on clean coal technologies and ensure effective carbon capture and storage. The clean coal technologies include the safe disposal and beneficial utilisation of post combustion products – the CCPs.
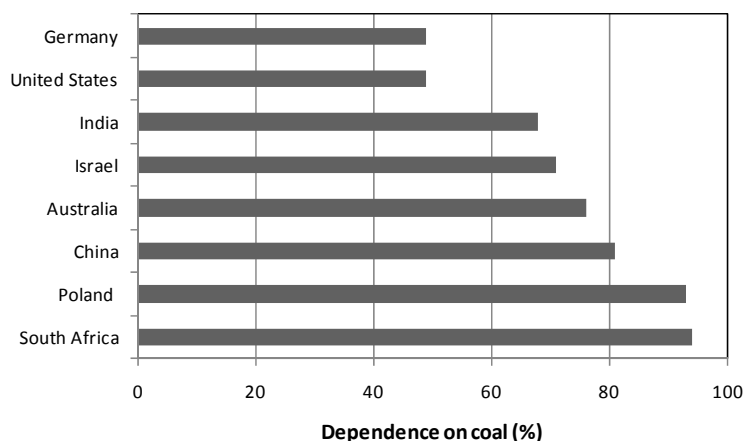
**Figure 1.** Countries depending on coal for their energy needs.

Sources, types and basic characteristics of CCPs

The Ash Development Association of Australia has recently updated the definitions of CCPs as follows (ADAA, 2009):

Fly ash (FA) - the non-combustible oxidized elements, light to mid-grey in colour, with sphere-shaped particles ranging in size from less than 1 μm to 200 μm that exit the combustion chamber in the flue gas and is captured using electrostatic precipitators, filter baghouses, or wet scrubbers (Heidrich, 2003). FA has typical pozzolanic characteristics (siliceous, or siliceous and aluminous material).

Bottom ash (BA) - agglomerated ash particles formed in pulverized coal furnaces that are too large to be carried in the flue gas stream and impinge on the furnace walls or fall through open grates to an ash hopper at the bottom of the furnace. Bottom ash is typically grey to black in colour, is quite angular, and has a porous surface structure.

Fluidised bed combustion (FBC) ash - is formed when fine coal is burnt in the presence of crushed limestone as a bedding material in fluidized form. The FBC is a technology employed to limit the amount of S released into the atmosphere while burning S-rich coal. Sulphur dioxide (SO_2) released during combustion is converted to calcium sulphate ($CaSO_4$) through its reaction with the calcined limestone. Fluidized bed furnaces burn coal at lower temperatures (815 - 870°C) than the conventional coal fired furnaces (1400 - 1600°C). The chemical reactions involving the limestone charge in a fluidized bed boiler can be described by the following equations:

$$CaCO_3 \rightarrow CaO + CO_2 \qquad (1)$$
$$CaO + SO_2 \rightarrow CaSO_3 \qquad (2)$$
$$2CaSO_3 + O_2 \rightarrow 2CaSO_4 \qquad (3)$$
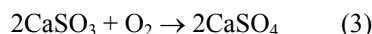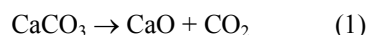
Because of its relatively low cost, the FBC technique has become widely used for reducing SO_2 emissions from electricity-generating plants. Existing coal fired power plants can be modified

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to FBC, and therefore present a simple option for bringing older plants into compliance with clean air legislation (Wang *et al.*, 1994).

Flue-gas-desulphurization

(FGD) ash - is the residue of alkaline scrubbing of sulphur oxides from flue gases of coal-fired power stations. A range of amendments including lime and ammonia are used to trap sulphur oxides, resulting in a range of FGD products. For example, FGD gypsum is obtained in the desulphurization of flue gases with lime or limestone suspension. Similarly, ammonia FGD is produced by reacting ammonium hydroxide with SO_2 to form ammonium sulphite, which is oxidized to ammonium sulphate. Apart from over 95% SO_2 removal capacity, this technology can also reduce the emission of other acid gases like sulphur trioxide and hydrogen chloride (Srivastava, 2000).

The chemistry of the production of $(NH_4)_2SO_4$ from boiler flue gas is very similar to the chemistry of wet limestone FGD. SO_2 from the flue gas is absorbed in the spray tower by water according to the equation:

$$SO_2 + H_2O \longleftrightarrow H_2SO_3 \qquad (4)$$

The H_2SO_3 is then reacted in a reaction tank with ammonia to form $(NH_4)_2SO_3$ and NH_4HSO_3:

$$H_2SO_3 + 2NH_3 \longleftrightarrow (NH_4)_2SO_3 \quad (5)$$
$$H_2SO_3 + (NH_4)_2SO_3 \longleftrightarrow 2NH_4HSO_3 \quad (6)$$
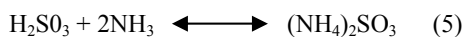
$(NH_4)_2SO_3$ and NH_4HSO_3 are also oxidized in the absorber (forced oxidation) to form $(NH_4)_2SO_4$ and NH_4HSO_4. The NH_4HSO_4 is neutralised in the presence of ammonia and water to form $(NH_4)_2SO_4$:

$$NH_4HSO_4 + NH_3 + H_2O \longleftarrow$$
$$(NH_4)_2SO_4 + H_2 \longleftarrow \qquad (7)$$
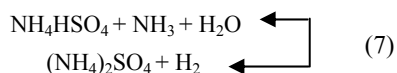
The fuel and S-capturing sources dictate the composition of these by-products in the coal industry. For example, the FBC ash is highly alkaline because of the presence of unspent sorbent, and also contains anhydrite, thus has potential to be used as liming material and S fertilizer; whereas FGD gypsum is nearly neutral and primarily used as a source of S.

In supplying the power requirements for Australian households, around 14.6 Mt (million tonnes) of CCPs are produced annually of which about only 1.787 Mt is utilized primarily in the construction industry. In Australasia, about 85% of the current "beneficial use" of fly ash is for partial cement replacement (between 10 & 20%) to enhance the properties of concrete and other building materials. Only about 0.5 Mt (3%) is used for non-cementitious applications, which include agriculture and environment (ADAA, 2008). Similarly, ash utilization as a percentage of total ash generated in different countries amounts to around 85% in West Germany, 73% in Denmark, 60% in France and UK, 50% in Poland, 32% in US, 25% in China and 15% in India (Sinha and Basu, 1998). However, there is a high potential for greater utilisation of these CCPs in Australia and worldwide.

Properties of coal combustion products

The physical and chemical properties of CCPs depend upon a number of factors, including the origin and the type of coal burnt, boiler conditions, type and efficiency of the emission controls and nature of sorbents used to trap S (Adriano *et al.*, 1980; Stout *et al.,* 1998; Wang *et al.*, 2006), but certain characteristics tend to be similar in most ashes. Chemically, CCPs are mainly

silico-aluminate glasses, though some mineral materials may also be present. Based on the chemical composition, FA is grouped into two classes – F and C (ASTM, 1994). They primarily differ in the amount of calcium and the silica, alumina, and iron content in the ash, which also vary among the types of coal used (Table 1). Class F FA is highly pozzolanic and has total calcium content typically ranging from 1 to 12 %, mostly in the form of calcium hydroxide and calcium sulphate. In contrast, Class C FA contains calcium content as high as 30 to 40 %. Another difference between Class F and Class C is that the amount of alkalis (combined sodium and potassium) and sulphates (SO_4) are generally higher in the Class C fly ashes than in the Class F fly ashes. Countries like United States and India, which produces Class C fly ashes, need to strictly implement clean coal technologies like FBC and FGD for this reason. In Australia, the majority of ash produced is categorised as Class F – being mainly silica and alumina (80-85%) and less than 10% CaO (Table 1).

Table 1. Normal range of chemical composition for fly ash produced from different coal types (expressed as percentage by weight). ASTM (1994).

Component	Bituminous	Sub-bituminous	Lignite
SiO_2	20-60	40-60	15-45
Al_2O_3	5-35	20-30	10-25
Fe_2O_3	10-40	4-10	4-15
CaO	1-12	5-30	15-40
MgO	0-5	1-6	3-10
SO_3	0-4	0-2	0-10

Generally, the CCPs are mainly composed of silt-sized materials having a diameter from 0.01 - 100 μm (Kula *et al.*, 2002; Peng *et al.*, 2004). When compared with mineral soils, FA has lower values for bulk density, hydraulic conductivity and specific gravity. Both crystalline (mullite) and amorphous (glass) phases have been identified by X-ray diffraction in fly ash (Mattigod *et al.*, 1990; Karayigit and Gayer, 2001).

The chemical properties of CCPs will largely be determined by the metal oxides (Si, Al, Fe, Ca, Mg, Na, K) that are surface adsorbed during particle formation (Terman *et al.*, 1978; Adriano *et al.*, 1980). Most of these elements can substitute into the iron pyrite structure, and coals higher in pyrite therefore tend to produce CCPs which contain higher levels of these elements. The behavior of volatile elements such as Se and Hg is highly dependent upon the burning conditions within the boiler and the sorbents used for capturing S (Punshon *et al.*, 2003). During the combustion and subsequent cooling process many different metal oxides can precipitate and concentrate on the surfaces of fly ash particles. Based on reactivity and surface electric charge, three groups of solid components have been identified in fly ash (Terman *et al.*, 1978; Adriano *et al.*, 1980; Table 2).

Table 2. Groups of solid components in fly ash (Adriano *et al*., 1980).

Groups	Properties	Components
Group I	Low water reactivity , possess surface charge	Oxides of Si, Al, Fe and Ti
Group II	Adsorption to oxides	Metals and metalloids
Group III	High water reactivity	Oxides of Ca, Mg, K, Na, Ba, SO_3, Gypsum

The above mentioned physical and chemical properties of CCPs have driven coal industries and environment

researchers to explore the possible applications as part of the sustainable utilization strategies of these mine derived resources.

Application of coal combustion products

Currently, CCPs are used extensively in construction and agricultural industries. In the construction industry, they are used mainly as a source of concrete, roofing material and road surface sealing (Chugh *et al.*, 2006). The various types of CCPs and their potential applications are listed in the Table 3. In agricultural industries, they are used primarily as an amendment to improve the physical and chemical properties of soil, as a source of liming material to ameliorate soil acidity and as a nutrient source to supply calcium and sulphur (Heidrich, 2003; Wang *et al.*, 2006).

About 85% of the current use of FA is for partial cement replacement (10-20%) to enhance the properties of concrete and other building materials. The BA is used as a sand replacement, aggregate for lightweight blocks, a road-base component, for agricultural drainage mediums and as an engineered bulk fill. The pozzolanic property of FA means in finely divided form and in the presence of moisture, it could chemically react with calcium hydroxide at ordinary temperatures to form compounds that have cementitious properties. As a partial replacement of the sand and cement in concrete, FA economically enhances performance in regard to workability, shrinkage creep and durability to produce high-performance concrete (Kurita and Nomura, 1998; Bilodeau and Malhotra, 2000).

The idea of utilizing CCPs in agriculture has originally arisen as a result of their role as a nutrient supplement in soils low in Se, Mo, Cu, Zn, or B (Page *et al.*, 1979; Adriano *et al.*, 1980; Kesh *et al.*, 2003; Yunusa *et al.*, 2006). The CCPs in general and FA in particular have a considerable content of K, Ca, Mg, S and P (Page *et al.*, 1979; Adriano *et al.*, 1980; Singh *et al.*, 1997; Yunusa *et al.*, 2006), which help in increasing plant growth and nutrient uptake.

Much research and development has been carried out in the past three decades on the use of fly ash in agriculture (Page *et al.*, 1979; Stehouwer *et al.* 1996; Stout *et al.* 2003; Wang *et al.*, 2006), where the potential of CCPs as liming agent, source of plant nutrients, and soil modifier has been exploited. The uptake or enrichment of various nutrients and toxic trace elements (Table 4) in soil after CCPs amendments has been investigated, and crop produce has been found safe for consumption (Sen *et al.*, 1997).

The agricultural use of CCPs highly depends on the nature of parent coal used and coal combustion technologies used for power generation (El Mogazi *et al.,* 1988; Wang *et al.* 1994). The agricultural use of CCPs has often been assessed in relation to its effects on: (1) crop yield and establishment; (2) uptake and accumulation of nutrient and non-nutrient elements; and (3) toxicity levels of trace elements (Table 4).

The CCPs are also used for various environmental applications that include: (a) Phosphorus retention; (b) Heavy metal immobilisation; (c) Acid mine drainage (AMD) mitigation and mine site reclamation; and (d) Carbon sequestration. For example, Stehouwer *et al.* (1995) demonstrated the value of CCPs as an amendment for coal refuse piles and non-agricultural lands, especially for reclaiming mined areas. Similarly, Gitari *et al.* (2006) examined the value of CCPs in mitigating AMD.

Table 3. Various types of CCPs - their major constituents and potential uses.

Type	Major constituents	Potential areas of major use
Fly ash	Si, Al, Fe, Ca (CaO, MgO, SiO_2, K_2O, Al_2O_3, Fe_2O_3)	Cement replacement in concrete/grout, structural fill, flowable fill, waste stabilization, surface mine reclamation, soil stabilization, road based, mineral filler, Si and Ca source
Boiler slag	Si, Al, Fe, Ca (CaO, MgO, SiO_2, K_2O, Al_2O_3, Fe_2O_3)	Blasting grit, roofing granules, snow and ice control, mineral filler, construction backfill, water filtration, drainage media
Bottom ash	Si, Al, Fe, Ca, S ($CaSO_4$, CaO, $CaSO_3$, MgO, SiO_2, K_2O, Al_2O_3, Fe_2O_3)	Concrete block, road sub-base, snow and ice control, structural fill, waste stabilization, pipe bedding, cement manufacture, liming material, Si, Ca and S source
FGD material	Si, Al, Fe, Ca, S ($CaSO_4$, CaO, $CaSO_3$, MgO, SiO_2, K_2O, Al_2O_3, Fe_2O_3)	Wallboard, stabilised road base/sub-base, structural fill, surface mine reclamation, underground mine injection, livestock pad, low permeability liner, synthetic aggregate, sludge stabilization
FBC material	Si, Al, Fe, Ca, S ($CaSO_4$, CaO, Quartz, gypsum)	Slow release fertiliser, liming material

Bioavailability of nutrients and heavy metals

Application of CCPs to soil influences the bioavailability of nutrients and heavy metals by acting as a source and also by affecting their transformation in soils (Table 5). For example, depending on the origin, CCPs contain appreciable amounts of nutrients such as sulphur, calcium and magnesium and heavy metals such as cadmium, chromium and mercury, thereby acting as a source of these elements (Table 4). Similarly, the application of CCPs is likely to affect soil properties such as pH and cation exchange capacity, thereby influencing the reaction and transformation of nutrients and heavy metals.

Bioavailability refers to how much of a chemical is available to a living biota including plants and soil microorganisms. (Naidu *et al.,* 2008) However, the bioavailability of a chemical defines the relationship between the concentration of the chemical in the terrestrial environment and the level of the chemical that actually enters the receptor causing either positive or negative effect on the organism. Bioavailability is species-specific because the dose which reaches an organism's target organs or tissues, and results in a biological response, may vary among receptors (Stokes *et al.*, 2005). Bioavailability is also often referred to as the extent to which a chemical can desorb, dissolve, or otherwise dissociate from the environmental medium in which it occurs

to become accessible (i.e. bioaccessibility) for absorption (Alexander and Alexander, 2000). Chemical bioavailability is now considered an important issue in the environment because the availability of chemicals may be mitigated once the chemical comes in contact with the soil and sediment. For this reason, both fertility status of soils and risk assessment of contaminated sites require quantification of chemical bioavailability much like any other parameter in fertilizer recommendation and risk calculations (Hrudey *et al.*, 1996). In both fertilizer recommendation and contaminated site assessment, bioavailability addresses the fundamental issue of exposure of the element to a receptor. However, exposure is not dictated by the total concentration of the element in the environmental media, but rather by the fraction of the total concentration of the element that is biologically available. Hence, exposure can only occur following the release (e.g. desorption) of the element from the soil particle and if the element is then transported to the receptor. The amount of an element in soil that is bioavailable depends on a variety of factors including the properties of both the element and the soil environment (Adriano *et al.*, 2004).

Nutrients

Numerous studies have examined the value of CCPs as a nutrient source (Table 4). The major nutrient elements in CCPs include Si, Al, Fe, Ca and S, together with lesser amounts of Na, Mg, B, Sr and K. For example, FBC and FGD ashes have Ca and Mg contents ranging from 13% to 39% and from 0.1% to 16%, respectively depending on whether the sorbent is calcite or dolomite. Due to the presence of unspent sorbent, FBC ash is usually highly alkaline (pH$_{water}$ 10.5-12.5) with significant neutralization potential. It has

been reported that the best agricultural use of FBC ash is as a liming source to overcome the problems associated with soil acidity (Terman *et al.*, 1978; Stout and Priddy, 1996; Wang *et al.* 1994). The S content of FBC and FGD ashes is also relatively high, being mainly in the form of CaSO$_4$ (anhydrite). Therefore, these two are a major source of both Ca and S for plant nutrition in addition to relatively high liming value (Wang *et al.* 1994). Compared with Ca and S, the amounts of N, P and K in CCPs are negligible. The micronutrient content in CCPs is low except for boron (B) that ranges from 36 to 1360 mg kg^{-1} (Table 4). Boron is an essential mineral nutrient for all vascular plants. The functions of B are primarily extracellular, which relates to lignification and xylem differentiation. Some of the CCPs such as FBC ash also contain small amounts of selenium (Se, 0.16 - 5.6 mg kg^{-1}) which is an essential nutrient for animals but not for plants. Due to the oxidizing conditions to which these elements are exposed during combustion, Fe, Mn, Cu and Zn probably occur as oxides in FBC ash, and B and Mo as borates and molybdates (Table 5).

The presence of S in FBC and FGD ashes as anhydrite (CaSO$_4$) or gypsum (CaSO$_4$.2H$_2$O) after hydration makes these CCPs the major S source in S-deficient soils. Gypsum, including industrial by-products, such as phosphogypsum, has been successfully used as an S fertilizer to increase the yields of winter wheat, rice and pasture. To date, data on the use of these two CCPs as a S fertilizer is limited, although Terman *et al.* (1978) demonstrated that FBC ash is an effective S source for growing corn and peanuts. Approximately 50% of S in slaked FBC ash is present as sparingly soluble ettringite, which can act as a slow-release S fertilizer (Wang, 1996).

Table 4. Selected references on nutrient and heavy metal concentrations in CCPs

CCPs	Nutrients (g kg^{-1})								Trace elements (mg kg^{-1})						Ref.*
	P	**S**	**Al**	**Ca**	**Fe**	**Mg**	**Na**	**B**	**As**	**Cd**	**Cr**	**Hg**	**Pb**	**Se**	
Fly ash	-	-	-	-	-	-	-	1.69	7.0	0.1	38	1.3	15	2.9	**1**
	0.956-1.002	-	110-130	5.3-5.7	82-100	4.977-5.494	2.322-2.553	0.003-0.0036	116-129	2.8-3.5	155-169	0.27-0.45	60-63	12-17	**2**
	1.388-1.432	1.26-1.3	75-117	13-14	41-73	5.179-5.426	4.183-4.420	0.0199-0.0211	112-125	3.0-5.0	97-155	0.22-0.31	247-263	8.4-11	**3**
	0.4-8	1-15	1-173	1.1-222	10-290	0.4-76	0.1-20.3	0.01-6.18	2.3-6300	0.7-130	10-1000	0.02-1.0	3.1-5000	0.2-134	**4**
	0.2315	2.738	4.136	8.435	13.51	4.66	0.37	0.298	-	2.8	26.8	-	2.5	-	**5**
	3.760	0.948	147	27.4	90.9	8.87	2.39	0.056	22.3	0.52	69.2	-	49	2.26	**6**
FBA	-	-	13.0	300	55.0	18.0	1.0	-	-	<2	50.0	-	85.0	-	**7**
	0.875	62.0	18.0	254	36.0	6.0	7.0	1.36	6.5	<0.1	<0.1	-	<2.0	<3.0	**8**
	0.1	86.4	27.5	244	20.8	163	9.5	0.206	46.7	3.5	17.5	-	28.0	2.3	**9**
	0.2	38	0.1	391	5.0	5.0	-	1.328	8.1	0.2	33	-	88.0	3.3	**10**
FGD	0.573	85	25.5	146	85	3.7	0.722	0.356	107	<0.2	51	-	15	-	**11**
	-	67.1	19.6	260	16.5	27.1	-	0.194	118	<0.1	123	-	139	<6.0	**12**
	0.2	182	8.0	201	0.1	0.4	-	0.131	6.3	0.7	15.0	-	100	2.3	**13**
	-	205.4	3.3	269.1	-	4.5	-	-	1.08	<0.1	9.70	0.658	4.08	0.84	**14**

*References: (**1**) McDowell (2005); (**2**) Punshon *et al*. (2002); (**3**) Adriano *et al*. (2002); (**4**) Sharma and Kalra (2006); (**5**) Sajwan *et al*. (2007); (**6**) J.Jankowski *et al*. (2006); (**7**) Karapanagioti and Atalay (2001); (**8**) Wang *et al*. (1994); (**9**) Stehouwer *et al*. (1996); (**10**) Wright *et al*. (1998); (**11**) Ahn and Mitsch (2001); (**12**) Chen *et al*. (1995); (**13**) Wright *et al*. (1998); (**14**) Wang *et al*. (2008).

Table 5. Selected references on CCP-induced mobilization of nutrients and heavy metals in soils.

Nutrients	CCP source	Observations	Reference
		Nutrients	
Nitrogen	FA and BA	Although applications of CCPs had little influence on fertilizer N, application of BA caused substantial decreases in the total N content in soil solution through the mobilization of organic N and N losses in the forms of amino sugars, amino acids, and hydrolysable NH_4^+ could account largely for losses of total N in BA-amended soils, resulting an increase in soil pH.	Stuczynski *et al.* (1998)
	FA	FA is low in N; co-composting FA with biosolid increases the supply of N	Alva *et al.* (1999)
	FA	FA is low in nitrogen but increased the mineralization of organic N. Organic matter rich soils or N-fixing plants with an apparent heavy metal-tolerance can be helpful as the early colonisers of FA dumps and nearby areas.	Gupta *et al.* (2002)
	FA	Gypsum-FA mixture application (25 tons ha^{-1}) increased the maximum rice grain yield by 8%, thereby decreasing N application level to about 50 kg N ha^{-1} to produce the target yield.	Lee *et al.* (2003)
	FA	Enhanced N release from cow dung when vermicomposted in the presence of FA.	Battacharya and Chattopadhyay (2004)
	FA	FA is an important source of alkalinity in the upper 0 to 5 cm of lignite containing lake sediments that enhanced plant growth and led to enrichment of the sediment with N from organic matter derived from plant material	Chabbi and Rumpel (2004)
	FA	Integrated use of FA, bluegreen biological fertilizer and N fertilizer improved growth, yield and mineral composition of the rice plants besides reducing the high demand of N fertilizers.	Tripathi *et al.* (2008)
	FA	Addition of FA to alkaline treated wastewater sludge decreased the rate of mineralization of organic N in the sludge, thereby increased the residual value of sludge as a N source	Topac *et al.* (2008)
	FGD gypsum	Application of FGD gypsum with N fertilizer promotes the uptake of N by corn in S-responsive soils, thereby decreasing the amount of N required for high-yield corn production and reducing the degradation of water quality associated with oversupply of N	Chen *et al.* (2008)

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Nutrients	CCP source	Observations	Reference
Phosphorus	FA and BA	While alkaline FA had higher sorption maxima, BA and acidic FA had very low sorption capacity at low concentrations. Results suggested that alkaline FA may be a promising amendment for coarse sand bed to enhance P removal.	Cheung et al. (1994)
	FA	P mobilisation enhanced by organic acids and microbial activity in swine manure amended with fly ash; B was highly soluble at the highest application rate and was detrimental to plant growth	Vincini et al. (1994)
	FA	Immediate and long-term decreases in P desorption occurred in the incubation study at all ash rates when greater than 500 mg P kg^{-1} were added but FA had little effect on P desorption at P rates less than 50 mg P kg^{-1}	O'Reilly and Sims (1995)
	FA	Coapplications of FA and animal manure products stabilized manure P, thereby allowing land application rates needed to fulfil plant N requirements without causing water quality impairments.	Dao (1999)
	FA	The FA amendment retarded NO_3^-, NH_4^+, and P leaching in sandy soils and can be a useful tool for improvement of nutrient management in sandy soils.	Pathan et al. (2003)
	FGD gypsum	Treatment of high P soils with FGD gypsum decreases water-extractable P by conversion to soil IP fractions that are stable with time, it does not decrease plant production and suggests that the potential for P export in surface runoff may be reduced for several years.	Stout et al. (2003)
	FBC	Increased P loss – solubilisation of organic P due to an increase in soil pH resulting from free CaO content	McDowell (2004)
	Furnace slag and FA	The expected lifetime of constructed wetlands for P removal is likely to be increased with the use of furnace slag and FA	Xu et al. (2006)
	FA	Application of FA to rice cultivation increased available P resulting from high content of P (786 mg P kg^{-1}) in the applied FA	Lee et al. (2007a)
	FA plus phosphogypsum	The mixture significantly reduced water-soluble P (W-P) in the surface soils by shifting from W-P to iron bound-P (Fe-P), calcium bound-P (Ca-P) and aluminium bound-P (Al-P) during rice cultivation, thereby reducing P loss from paddy soils.	Lee et al. (2007b)
	FA	Addition of FA to pasture soil increased the mineralization of organic P	McDowell et al. (2008)
	FA	Sand amended with FA as filter media in bioretention cells increased P removal	Zhang et al. (2008)

Continued….

Nutrients	CCP source	Observations	Reference
Sulphur, Calcium, Potassium, Magnesium and Sodium	FA	Released Mg at rates comparable to most Mg fertilisers	Hill and Lamp (1980)
	FBA	Water soluble S is up to 50% with slow dissolution of remaining S; most of K is in the soluble form; dissolution of gypsum and portlandite in FBA increased soluble Ca concentration, less than 50% of the Na salts in FBA were water-extractable	Wang *et al.* (1994)
	FBC	Leachate Mg and S concentrations increased as $MgSO_4$ ion pair	Stehouwer *et al.* (1995)
	FGD	Mobility of Ca, Mg and S increased with increasing depths of FGD application in soil. 90% of leachate S was present as SO_4-S	Stehouwer *et al.* (1996)
	FA	Soluble Ca increased gradually over time under field conditions and increased sharply under alternate wet-dry conditions in a lignite mine spoil	Seoane and Leiros (2001)
	FA	Boron is highly leachable (17-64%) from alkaline FA with, but not completely pH dependent	Jankowski *et al.* (2006)
Heavy metals			
Zinc, Iron and Manganese	FA	Bacterial activity in FA amended soil increased mobility of Zn, Fe and Mn initially, but slowly decreased as the incubation period increased	Tiwari *et al.* (2008)
Cadmium and Antimony	FA	Increased the water extractable fractions of Cd and As	Fernández-Turiel *et al.* (1994)
Aluminium, Chromium and Vanadium	FA	Increased the water soluble bioavailable fractions of Al, Cr and V	Gomez *et al.* (2007)
Copper and Zinc	FA	Sequential fractionation indicated 2.6% of Cu and 3.4% of Zn in FA was water soluble.	Soco and Kalembkiewicz (2007a)

Continued….

Nutrients	CCP source	Observations	Reference
Heavy metals			
Antimony	FA	22-36% of readily soluble Sb in FA amended soil at acidic pH	Miravet *et al.* (2006)
Nickel	FA	Biological dissolution (Microbial redox actions or mammalian phagocytosis) influences Ni mobility in FA amended soils	Wong *et al.* (1997)
Chromium	FA	Under extreme environmental conditions (oxidizable or reducible) FA increases Cr mobility from 8.2% to 52.4% Cr.	Soco and Kalembkiewicz (2007b)
Arsenic	FA	Phosphate in FA displaced As, thereby increasing its mobility	Qafoku *et al.* (1999)
Molybdenum and Selenium	FA	Increased Mo and Se availability in soil at elevated pH	Carlson and Adriano (1993)

Therefore, slaked FBC ash shows potential to be used as a basal S fertilizer in soils prone to severe leaching, which are common in some high rainfall areas of New Zealand and in soils with low anion retention capacities. For example, results from a field study in the peat soil indicated that ettringite-S in slaked FBC ash was less affected by leaching loss than gypsum and resulted in longer-term pasture yield S responses to FBC ash treatments (Wang, 1996). This was supported by herbage S analysis where, 8 months after application, herbage S contents in the high rates of FBC ash treatments (6616 and 26462 kg ha^{-1}) were significantly higher than the control. Hill and Lamp (1980) demonstrated that in Australian soils, FA released magnesium (Mg) at rates comparable with established Mg fertilizers.

A number of studies have examined the value of CCPs in the immobilization of P (Cheung and Venkitachalam, 2000; Stout *et al.*, 2003; McDowell, 2004 & 2005; Table 5). Loss of P through leaching and surface runoff, especially in sandy soils is a major environmental issue in many countries including Australia, resulting in the eutrophication of surface waters. For example, concentrations of P in runoff from agricultural catchments in southern Australia are high and well above national and international limits (Cox *et al.*, 2005). They argue that P loss is a serious problem in most parts of Australia due to its unique soil (sandy texture) and climatic (xeric; i.e., strong seasonal wetting and drying cycles) conditions. Cheung and Venkitachalam (2000) reported that coarse, sandy soil such as those found in Perth, Western Australia, exhibit low attenuation capabilities for P during effluent infiltration.

Various CCP sources including FA and BA have shown potential as soil amendments to decrease soil inorganic P solubility. For example, Stout *et al.* (2000) reported that FBC ash has consistently reduced concentrations of water-soluble P in a number of soils with high concentration of soluble P. They found that amendment with FBC ash resulted in a shift from readily available resin P and less available NaOH-extractable Fe and Al-bound P fractions to HCl-extractable Ca-bound P, which can be attributed to their neutralizing capacity. However, considering the high treatment rates (22 tons ha^{-1}) required to significantly reduce readily available P in soils, Codling *et al.* (2002) suggested that FBC ash may not be suitable for field application to sequester P in high P soils.

The FBC ash has also been tested in a number of studies to reduce solubility and mobility of P in soils with high P concentration and in P-rich organic wastes (Codling *et al.*, 2002; Dou *et al.*, 2003). In a packed column leaching study involving dairy manure, Elrashidi *et al.* (1999) reported that P in leachate in FBC ash treated column was reduced by more than 80% compared with the control treatment containing dairy manure only. In a laboratory incubation and extraction study, Dou *et al.* (2003) found that FBC ash applied at a rate of 400 g kg^{-1} reduced readily soluble P by 50-60% in P-rich manures including dairy, swine and broiler litter.

Seshadri *et al.* (2009) compared the effect of various sources of CCPs including FA, FBC and FGD ashes on P sorption in a variable charge soil. The increase in P sorption with the addition of CCPs is attributed to an increase in soil pH (Figure-2) and an increase in the concentration of aluminium (Al), Iron

(Fe) and Ca in soil solution resulting in the formation of insoluble Al-P, Fe-P and Ca-P (McDowell, 2004). The decrease in P sorption with increasing levels of FGD gypsum is attributed to the decrease in soil pH. Bolan *et al.* (2008) examined P leaching as affected by various liming materials including FBC ash in a variable charge soil (Table 6). FBC ash decreased both bioavailable P as measured by Olsen P and leaching of P.
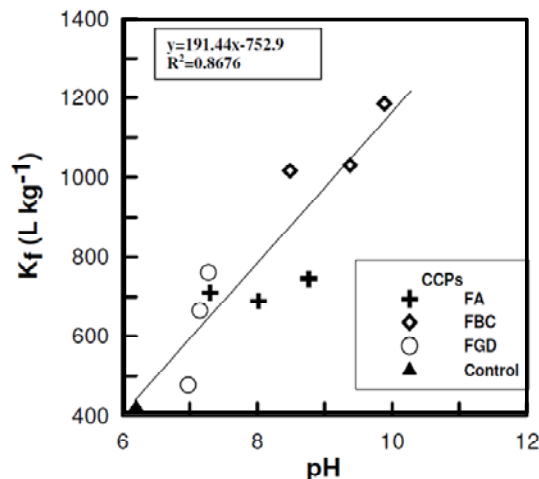

Figure 2. The relationship between soil pH and increase in phosphate sorption (as measured by distribution coefficient - Kf) as affected by various Ca containing soil amendments.

Table 6. Effect of various liming materials on bioavailable P and leaching of P.

Treatment	CCE (%)*	Rate (kg ha^{-1})	Olsen P (mg kg^{-1})	Leaching (kg ha^{-1})
Control	-		165	37.65
FBA	42	600	35.2	4.52
Dolomite	114	220	28.6	3.48
Lime stone	100	250	15.4	2.85

However, Mc Dowell (2004) observed increased P losses in New Zealand pasture soils when soil pH was raised with the application of FBC ash which has been attributed to the solubilisation of organic P due to free CaO in this ash by-product. He consequently concluded that ash could be useful as a supplement or alternative to lime in cropping soils where the pH is commonly maintained at a higher level and may, in these soils, prove beneficial in mitigating P loss (McDowell, 2005). Similarly, although most CCPs contain insignificant N

amount, application of CCPs with organic amendments such as biosolids has been shown to increase the mobilization of N by inducing the mineralization of organic N (Stuczynski *et al.*, 1998).

Heavy metals

Principally, the amount of trace elements (including heavy metals) in CCPs, excluding B is found within the range actually present in soils (Table 4). For example, Korcak and Kemper (1993) observed no phytotoxic effects of micronutrients when FBC ash was used as a liming source even at very high rates. However, the availability of micronutrients to plants depends not only on the amounts applied in FBC ash, but also on the soil properties and the specific crop being grown.

Although B concentrations in most CCPs (Table 4) are higher than those found in most soils, it is not toxic in most agricultural soils, unless supplied in excessive amounts by fertilizers. Wang (1996) reported that high application rate of FBC ash (up to 19, 185 kg ha^{-1}) in a field trial had not induced visual symptom of B toxicity in a white clover and ryegrass dairy pasture in a peat soil. However, Clark *et al.* (1999) reported that a soil mixed with more than 0.5% FBC ash resulted in significant dry matter reduction of maize in a pot experiment due to B toxicity. Crews and Dick (1998) observed B toxicity symptoms in plant tissue when red oak is grown in soil applied with FGD ash at two times or higher the lime requirement rate. Therefore, care should be taken when applying CCPs with high levels of B to sensitive crops such as cherry, peach, lupin, and kidney bean, especially when these crops are growing on sandy soils.

Stout *et al.* (2000) reported that the heavy metal content in CCPs is comparable to that of more traditional agricultural soil amendment products, such as lime and gypsum. In addition, the oxide form of heavy metals in FBC ash makes them much less available to plants than the organic forms in sewage sludge. However, any increase in the quantity or availability of these metals in soils should be carefully monitored using appropriate soil tests.

The value of CCPs as a viable option in immobilizing heavy metals in contaminated soils has been examined in many studies. For example, Ciccu *et al.* (2001) conducted a study using soils from an Italian mine site contaminated severely with heavy metals and showed decreased levels of heavy metals in percolating water from fly ash mixed soil, indicating that fly ash in such soils can lead to immobilization of heavy metal ions.

Kumpiene *et al.* (2007) demonstrated reduced leaching of Cu and Pb from contaminated soil using coal fly ash and peat as soil amendments. They observed that the amendments reduced the exchangeable metal forms, likely because of the formation of new mineral Cu- and Pb-bearing phases and the enhanced metal sorption due to increased amount of sorptive sites. They also observed reduced metal uptake by plants and reduced soil toxicity to microorganisms. This was attributed to the rise of soil pH and the lowered metal mobility due to fly ash additions.

Stehouwer *et al.* (1995) observed that FBC ash reduced leachate concentrations of Al, Fe, Mn and Zn that are frequently phytotoxic in acid soils. Decreased solubility and mobility of these metals would also improve surface and drainage water quality.

CONCLUSIONS

The recycling of CCPs into construction and agricultural related applications can reap substantial environmental benefits. These include:

- Waste stream reduction and associated reductions in requirements for landfill.
- Contribution to the conservation of resources such as gypsum, limestone and natural gas which would otherwise be used in cement production.
- Reduction in Greenhouse Gas (GHG) emissions from cement production of almost 1 tonne of CO_2 per tonne of cement.
- Decrease in fertilizer application resulting from reduced losses

Land application of CCPs affects the bioavailability of nutrients and heavy metals by both acting as their source and sink in soils. Some of the CCPs are rich in S and Ca thereby acting as a source of these nutrients. They also control the transformation of N and P through immobilization and mineralization reactions. Similarly, CCPs can act as a source of heavy metals such as B and affect their reactions by altering soil solution chemistry including pH and ionic strength. Thus, CCPs can be used to manage the bioavailability of nutrients and heavy metals, thereby enhancing soil chemical fertility and mitigating metal contaminated soils.

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