# FLY ASH IN AGRICULTURE - MODERN APPLICATIONS OF COAL COMBUSTION BY-PRODUCTS

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**Summary.** Although alternative energy sources are gaining increasing importance, fossil fuels, especially coal, play a significant role in the global energy production. Unfortunately, coal combustion generates a large amount of Coal Combustion Products (CCPs), including fly ash. Fly ash has substantial negative effect on environment, while its properties could make it a desired secondary raw material in many industry branches. Due to the large amount of fly ash produced in recent years, the researchers have been searching for new, unconventional methods of FA utilization.

Fly ash can be used in agriculture, because it has special physical and chemical properties. FA has a unique structure and contains almost all the nutrients necessary for proper plants growth and development. First of all, fly ash is used as a mineral fertilizer which improves the physical, chemical and biological properties of soils. It can also be applied as an agent, which increases plant growth and amount of the obtained yields. In addition, fly ash is used to reduce the amount of heavy metals accumulated in plants and to limit the spread of diseases.

Although fly ash application in agriculture has many benefits, there are some disadvantages connected with this application (for example heavy metals and radionuclides contamination of soils and surface waters, soil salinity). In addition, there is also risk associated with lack of information on the long-term effects of fly ash application on soil quality and environment. Therefore, it is necessary to continue research on this topic to clarify the effects of the fly ash addition to the soil on agricultural production and the environment.

In this publication the authors determined the usefulness of FA and the limits of its use in agriculture. They also presented the modern applications of CCPs in agriculture, as well as evaluated the benefits and risks associated with this type of FA application.

Key words: fly ash, coal combustion products, agriculture, soil quality, fertilization, soil contamination.

# INTRODUCTION

Although alternative energy sources are gaining increasing importance, fossil fuels, especially coal, play a significant role in the global energy production. Around  $3.5 \cdot 10^9$  Mg of coal is mined in the world annually, which accounts for almost 38% of the world's electricity source [Ram and Masto 2010]. In Poland, the production of electricity and heat is also based on the thermal processing of bituminous coal and lignite in power plants.

Unfortunately, coal combustion generates a large amount of wastes in the form of Coal Combustion Products (CCPs). This group of wastes includes fly ash, slag, ash-slag mixture, micro-spheres, bottom ash from fluidized bed, gypsum and other wastes from flue gases desulfurization. Among them, fly ash (FA) deserves special attention because it has a substantial negative effect on the environment, while its properties could make it a desired secondary raw material in many industry branches [Szponder and Trybalski 2009b].

FA is a mineral residue from coal combustion. It leaves the boiler with the flue gases and then is captured by dust collectors (mainly electro-filters). It was estimated that 5.5<sup>10<sup>8</sup></sup> Mg of FA is produced each year in the world (most of all in China, USA and India) [Ram and Masto 2010], while in Poland approximately 4.2<sup>10<sup>6</sup></sup> Mg was generated in 2009. FA shows a wide variation in their physical, chemical and mineralogical properties which depend on the nature of fuel (bituminous coal, lignite, biomass, etc.), conditions of combustion, type of emission control devices, storage and handling methods. Specific physical, chemical and mineralogical properties and massive formation of FA allows for its wide use as raw material in many industry areas. In the same time, disposal and storage of FA is associated with high costs and a considerable burden for the environment. Traditionally, most of this secondary raw material is used in building industry, ceramics, road construction or mining. In recent years new, unconventional methods of FA utilization were found in the chemical industry, environmental engineering or agriculture [Pandey and Singh 2010, Szponder and Trybalski 2009a].

In this publication the authors determined the usefulness of FA and the limits for its use in agriculture. They also presented some modern applications of CCPs in agriculture, as well as evaluated the benefits and risks associated with this type of FA application.

## PROPERTIES OF FLY ASH

Fly ash is inorganic residue from coal combustion in power boilers. FA has a high morphological, phase and chemical composition diversity depending on the use of different methods of combustion (conventional and fluidized bed boilers), the composition of fuels (bituminous coal, lignite, biomass), a high dispersion of minerals in fuels and the dynamics of thermal processes. There are three basic groups of FA – silicate fly ash (sFA), aluminium fly ash (aFA) and calcium fly ash (cFA) [Szponder and Trybalski 2009b]. The most important properties of fly ash are presented in Table 1 [Sobik-Szołtysek and Janecka 2006].

Designation	Unit	Fly Ash		
		Silicate	Aluminium	Calcium
Specific density	[kg/m <sup>3</sup> ]	2500 - 4500	2000 - 4000	2000 - 4000
Specific surface by Blaine	$[cm^{2}cm^{-3}]$	2250 - 2450	2250 - 2450	2250 - 2450
Permeability	[m/s]	$10^{-10} - 10^{-7}$	> 10-7	$10^{-11} - 10^{-8}$
SiO <sub>2</sub>	[% by weight]	38 - 58	40 - 50	25 - 56
A1203	[% by weight]	15 - 31	30 - 35	5 - 18
Fe <sub>2</sub> O <sub>3</sub>	[% by weight]	4.5 - 15	5-12	4.5 - 8
CaO	[% by weight]	1.7 - 10	2 - 4	12 - 41
MgO	[% by weight]	0.2 - 5	1-3	0.8 - 7
Na <sub>2</sub> O	[% by weight]	0.3 - 1.5	0.5 - 1.5	0.1 - 1.5
K <sub>2</sub> O	[% by weight]	0.3 - 3.7	1.5 - 3	0.25 - 3

Table 1. Selected properties of fly ashes [Sobik-Szołtysek and Janecka 2006]

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SO,	[% by weight]	0.2 - 2	0.4 - 1	3.1 - 10
Cr	[ppm]	90 - 240	80-110	100 - 110
Cd	[ppm]	0.2 - 0.7	0.8	< 2
Cu	[ppm]	80 - 190	55 - 75	40 - 100
Ni	[ppm]	30 - 200	-	-
Pb	[ppm]	20 - 380	50 - 80	25 - 45
Zn	[ppm]	30 - 1100	110 - 140	90 - 220
Roasting loss	[% by weight]	2 - 10	0.5 - 2	0.5 - 2

### **Physical Properties**

Generally, fly ash is light gray to black in colour (depending on the amount of unburned carbon and organic matter residue). Some time it can be light brown to dark brown in colour (mostly from brown coal and biomass combustion). FA consists of fine, glassy particles, which range in particle size from 0.01 to 100  $\mu$ m. Their composition is dominated by spherical grains (mineral or amorphous), either solid (pirospheres), hallow (cenospheres) or filled with smaller amorphous particles (plerospheres). These grains appear individually, or in the form of aggregates. In addition, there is a large group of irregular, highly porous, rounded or sharp-edged grains in FA (carbon residue and soot). FA has low bulk density, high surface area and light texture [Ahmaruzzaman 2010].

#### **Chemical Properties**

The major chemical components of FA include oxides of silicon, aluminium, iron and calcium (95 - 99%). In addition, FA contains secondary components in the form of oxides of Ti, P, Mg, S, Na and K (0.5 - 3.5%) and unburned carbon (roasting loss). This waste also contains trace elements like Mn, B, Ba, Cu, Sr, Ni, Cr, Zn, Cd, Co, Mo, V, Se, Pb, As, etc. (0.1 - 0.3%) and radioactive elements like <sup>40</sup>K, <sup>226</sup>Ra i <sup>232</sup>Th. The pH of FA is usually in the range from 4.5 to 12.0, depending on the sulfur content in coal and on combustion and desulphurization technology. Wastes in which the ratio of Ca to S is lower than 2.5 are acidic in nature, and those with a ratio higher than 2.5 are alkaline [Szponder and Trybalski 2009a, Pandey and Singh 2010, Feng i in. 2006].

#### **Mineralogical Properties**

In its mineralogical structure, FA contains primarily amorphous substances in the form of silicon-aluminium glass (80%). It contains also a few crystalline phases such as gypsum (CaSO<sub>4</sub> 2H<sub>2</sub>O), mullite (3Al<sub>2</sub>O<sub>3</sub> 2SiO<sub>2</sub>), quartz (SiO<sub>2</sub>), magnetite (Fe<sub>3</sub>O<sub>4</sub>), anhydrite (CaSO<sub>4</sub>), ettringete (3CaO Al<sub>2</sub>O<sub>3</sub> 3CaSO<sub>4</sub> 3 32H<sub>2</sub>O), opaline SiO<sub>2</sub>, hematite (Fe<sub>2</sub>O<sub>3</sub>), lime (CaO), chlorite, feldspar, and spinel (FeAl<sub>2</sub>O<sub>4</sub>) [Ahmaruzzaman 2010, Szponder and Trybalski 2009a].

### Fly Ash Properties Significant for Application in Agriculture

Because of its favorable physical and chemical properties fly ash has been used in agriculture and forestry for more than thirty years. The specific and bulk density, particle size, porosity, water holding capacity, surface area and chemical composition are the most important physicochemical properties of FA allowing for utilization in agriculture. FA contains most of the necessary plant nutrients (except of nitrogen and organic carbon, which are oxidized in the combustion process). This deficiency is compensated by high concentrations of phosphorus, which by reaction with aluminum, iron and calcium contained in the alkaline FA, can be easily absorbed by plants. Significant amount of macro- and micronutrients in FA utilized in agriculture improves soil fertility, which encourages the crops growth. Moreover, FA with large amounts of amorphous aluminosilicate glassy spheres is great addition to the clay soil, and considerably improves its properties. At the same time, calciumrich alkaline FA is very useful for neutralizing acidic soils. Because of these and other physical and chemical properties of FA, its application in agriculture improves soil fertility [Pandey and Singh 2010, Singh et al. 2010].

Despite these favorable characteristic, environmental concern has been raised as to the potential risk FA may pose to plants and consumers. These disadvantages are connected mainly with heavy metals presence in FA. Those metals can be accumulated in crops and may be poisonous to final consumers. Furthermore, traces of radionuclides contained in this waste present a risk to crops [Singh et al. 2010].

# APPLICATIONS OF FLY ASH IN AGRICULTURE

In agriculture, fly ash can be utilized in many different ways. First of all, it is used as a mineral fertilizer which improves the physical, chemical and biological properties of soils. Also, it can be applied as an agent which increases plant growth and the amount of obtained yields. In addition, FA is used to reduce the amount of heavy metals accumulated in plants and to limit the spread of diseases.

#### Soil Quality Improvement

The influence of fly ash application on physical, chemical and biological properties of soil and its quality has been carefully examined [Ram and Masto 2010, Singh et al. 2010, Pandey and Singh 2010, Ferreira et al. 2003, Ciećko et al. 2009, Właśniewski 2009, Fulekar 1993, Gracia i in. 1995, Phung et al. 1979, Lai et al. 1999, Menon et al. 1993, Kalra et al. 1997, Vincini et al. 1994].

FA addition to soil significantly alters its structure. Because FA particles are small and have specific shapes (e.g., hollow spheres), it causes the formation of pores and voids in the soil structure. The changes in soil structure are related to such changes in its physical properties as bulk density, porosity, hydraulic conductivity, water holding capacity and aeration. These properties have a direct impact on the nutrients availability in the soil, its biological activity, and plant germination and growth. Another property of FA, which improves soil quality, is the presence of pozzolanic minerals such as Ca and Si in FA. This property affects the soil bulk density, porosity and its ability to retain water [Ram and Masto 2010]. For example, research [Fulekar 1993] showed that the addition of a large dose of FA (600 th<sup>-1</sup>) to acid clay soil, causes a significant improvement in soil texture and its physical and chemical properties. An the same time, the addition of a large amount of FA (200 - 400 t.h<sup>-1</sup>) to sandy-clay soil results in a significant improvement of its bulk density, acidity, gas permeability and water holding capacity [Gracia et al. 1995].

The addition of FA to soil has a significant effect on its chemical properties. Fly ash, especially alkaline FA, contains large amounts of Ca and is used to reduce soil acidity. If FA contains significant amounts of silicate minerals such as mullite, it forms silicic acid, which neutralizes hydrogen ions in the soil. Adequate pH in soil has a significant effect on the chemical components bioavailability, and thus directly and indirectly affects plant growth [Ram and Masto 2010]. Fly ash successfully replaces limestone and dolomite in soil pH regulation. For example, some studies [Phung et al. 1979] showed that the addition of 1 kg of alkaline FA has the same effect on soil pH and calcium bioavailability as the addition of about 0.2 kg of pure CaCO<sub>2</sub>.

Fly ash also provides minerals which are essential for soil, such as P, K, B, Ca, Mg, Mn, Zn, carbonates, bicarbonates and sulfates. Micro and macro elements delivered to soil in the FA have a positive effect on plant growth and upgrade its agronomic properties [Ram and Masto 2010]. For example, Lai et al. [Lai et al. 1999] found out that the concentrations of Mg, B, K and P increased in the soil which contained about 5 - 10% of FA. Also, Menon et al. [Menon et al. 1993] noted that in the crops growing on the medium containing FA, the concentration of biogenic elements, such as K, Ca, Mg, S, Zn and B, is higher than in the traditionally grown plants.

An effect of FA on the soil's biological and biochemical properties has not been thoroughly studied. There is no information on the biological processes and the impact of too low or too high FA concentration on the soil's biological properties. Although FA does not directly affect the biological activity of the soil, it changes soil texture what may lead to intensification of biological processes in soil [Ram and Masto 2010]. For example, some studies [Kalra et al. 1997] showed that 5% concentration of FA in soil increased microbial activity, while addition of larger amounts of FA inhibited biological processes. However, research conducted by Vincini et al. [Vincini et al. 1994] showed that concentration of FA in soil higher than 10% still enhanced microbial activity in soil. The impact of FA on microbial activity is inconclusive. It is generally accepted that small amounts of FA have little effect on microbial activity and larger FA concentration in soil inhibits microorganisms.

### Plant Growth and Yield Increase

The application of fly ash for soil fertilization is associated with plant growth and yield increase. FA contains almost all minerals necessary in the metabolic processes of plants. The influence of FA application on plant growth and production yield rate has been studied by many researchers [Ajaz and Tiyagi 2003, Khan and Khan 1996, Singh and Agrawal 2010, Singh et al. 2010, Iyer and Scott 2001]. In most cases, the addition of FA to soil increases plant growth as well as the minerals and nutrients uptake.

For example, Khan and Khan [Khan and Khan 1996] conducted a study on the impact of FA on tomatoes growth. They were trying to determine the most suitable dose of FA in the soil. In the experiment they used the following doses of FA: 0, 10, 20, 30, 40, 50, 60, 70, 80, 90 and 100%. The research showed that in the soil which contained from 20 to 80% of FA, the growth of shoots and roots increased by 40 - 90%. In the sample which contained 100% of FA, plant growth increased by app. 5%. The most optimal soil contained 50 - 60% of FA.

In their studies Ajaz and Tiyagi [Ajaz and Tiyagi 2003] determined the effect of different concentrations of FA (0, 10, 25, 50, 75, 90 and 100%) on cucumbers growth and quality parameters (length, fresh and dry weights, leaf area). Parameters improvement took place when the soil contained 10 - 50% of FA. The fresh weight of cucumber increased maximally by 115% at the soil mixture which contained  $\frac{1}{4}$  of FA and  $\frac{3}{4}$  of soil. The production of cucumber decreased at the concentration of FA in the soil above 50%.

Other researchers [Singh and Agrawal 2010] examined the effects of different concentrations of FA addition to soil on the growth of three cultivars of mung bean. The use of fly ash had a positive influence on the mung bean growth and the crops productivity. 10% concentration of FA in the soil turned out to be the best for cultivars M. Jyoti and M. Janpriya (40.6 and 33.9% growth increase), while 5% concentration was the most beneficial for cultivar M. Jagriti (29.5% growth increase). The

researchers concluded that the differences in the effects of FA application on the growth of mung bean may indicate a genetic base for variability.

As it was demonstrated in the examples, the addition of FA to soil has various effects on plant growth and yields. These parameters depend both on the amount of added FA and on plant characteristics.

#### Stabilization of Soil Contaminated with Heavy Metals

Lately, increased attention has been paid to the possibility of stabilization (chemical immobilization) of soil contaminated with heavy metals by applying fly ash. Stabilization minimizes the mobility of heavy metals, so these contaminations are not transported into deeper soil layers and into groundwater any longer. In addition, after immobilization of phytotoxic trace elements it will be possible to restore fertility to highly contaminated soils [Singh et al. 2010, Pandey and Singh 2010, Ayala et al. 1998].

Research [Ciccu et al. 2001, Ciccu et al. 2003] showed that fly ash addition to soil bounces metals and reduces their transport susceptibility, as well as helps to restore the natural soil properties. Stabilization of metals is based on such phenomena as adsorption, complexation and (co) precipitation. It was found out that for the immobilization of heavy metals alkaline FA (high sorption capacity) and zeolites synthesized from FA could be used.

Kumpiene et al. [Kumpiene et al. 2007] investigated the use of a mixture of fly ash and peat as an additive to soils contaminated with heavy metals. They found that mobility and bioavailability of metals such as Cu and Pb in soil is significantly reduced by using this agent.

Other researchers [Cornell and Schwertmann 2003] proved that the iron oxides contained in the fly ash can absorb significant quantities of metals from soil. In this case, high soil pH is required, because the amount of contamination adsorbed by iron oxide decreases with decreasing pH.

Fly ash is an effective, inexpensive and environmentally friendly additive for stabilization of soils contaminated with heavy metals.

#### **Agricultural Diseases Control**

Fly ash can be successfully used in agricultural diseases control. Several studies were carried out in this field [Pandey et al. 2009, Narayanasamy and Gnanakumar 1989, Narayanasamy and Gnanakumar 2005, Sankari and Narayanasamy 2007, Eswaran and Manivannan 2007, Mendki et al. 2001]. These studies show that FA can be used as a potential insecticide in agricultural areas. FA could be also used as an active carrier in certain insecticide formulations like dust, wettable powder and granules [Pandey et al. 2009].

In their studies, Narayanasamy and Gnanakumar [Narayanasamy and Gnanakumar 1989, Narayanasamy and Gnanakumar 2005, Sankari and Narayanasamy 2007] confirmed the insecticidal properties of FA (especially FA from lignite) against pests such as Epilachna, Spodoptera, Lepidoptera and Coleoptera. They developed the FA application in pests control in rice, vegetables (eggplant, okra, tomato, cauliflower, bitter gourd, etc.), and stored grain. They also determined the bio-efficiency of FA-based pesticides. The most effective against insects were pesticides, which contained FA and turmeric or neem seed kernel.

Eswaran and Manivannan [Eswaran and Manivannan 2007] studied the effect of fly ash from lignite on viral disease of papaya leaves. They applied a treatment which included various concentrations of FA administered at different days after planting. It turned out that the most effective was

double application of around 2 kg of FA from lignite on the plant 90 and 120 days after planting. This treatment significantly reduced the amount of the virus and the disease spreading. The authors concluded that the use of FA from lignite has significantly improved plant resistance mechanism and increased the fruit production.

The study [Mendki et al. 2001] shows that fly ash can be used as a safe insecticide in the pulses storage. The addition of 1 kg of FA at 5000 kg of seeds protects them against pests (especially Callosobruchus chinensis) for 16-18 months.

These and other scientific researches confirm that fly ash can effectively control various pests infesting plants, especially vegetables, both in laboratory and field conditions.

#### Forestry

Fly ash can also be used in forestry. Primarily it can be used to change the acidic pH of forest run, especially in the forest which grows on soil with small amount of nutrients (e.g. sandy soils). Usually in this type of forest tree species such as P. deltoids, D. sissoo, Eucalyptus sp, Melia Azadirachta, Casuarina cunninghamiana miq., etc. are present. In his research, Riekerk [Riekerk 1984] proved that the addition of fly ash to poorly drained sandy soil can increase the pH of the run from 4.7 to 6.0 and can double the growth rate of pine trees.

FA can be used to increase biomass production. Soils with minerals and nutrients deficiency are fertilized by FA additives. FA may be applied as a filler for soils in forest nurseries [Pandey i in. 2009].

Additionally, certain species of trees can be planted on reclaimed FA landfills. During land reclamation, many species like D. sissoo, Albizia Lebbeke, Eucalyptus hybrid, Acacia and Tamarindus are planted on soils, which contain large amounts of FA. This brings mutual benefits. On one hand, the land contaminated with FA is restored. On the other hand, very fast-growing tree species, planted on landfills, provide large amounts of biomass, which can be used in industry, and bring economic benefits [Pandey et al. 2009].

#### Floriculture

It is advisable to use fly ash in floriculture and ornamental plant production. FA contains all nutrients which are necessary for proper plant growth. However, it also contains heavy metals which are toxic for living organisms. As ornamental plants are not consumed by humans and animals, they can be fertilized by FA, even if they contain heavy metals [Pandey et al. 2009].

FA can also be used for ornamental plants and storage of their cuttings, for pot cultivation, and especially for hydroponics cultivation. This type of cultivation traditionally uses sphagnum peat, pine bark, coir dust, perlite and vermiculite, which are generally acidic (pH app. 4.0) and contain limited amounts of minerals. Therefore, liming materials (dolomite, calcitic limestone, etc) are used to adjust the pH. Additionally, the shortage of minerals and nutrients is supplemented by the addition of artificial fertilizers. Since alkaline FA is widely available, it can be used to replace liming materials, previously used in the cultivation of ornamental plants. This innovative solution brings mutual benefits, because firstly it significantly reduces the cost of ornamental plants and flowers cultivation, and secondly it is a great method for ecologically and economically justified FA utilization [Pandey et al. 2009].

# RISKS CONNECTED WITH FLY ASH APPLICATION IN AGRICULTURE

Although fly ash application in agriculture has many advantages, there is a risk associated with it. The primary disadvantage of this utilization is the possibility of contamination of soils and surface waters with heavy metals and radionuclides, and change in soil salinity. In addition, there is also a risk associated with lack of information about the long-term effects of fly ash application on soil quality and environment.

### **Heavy Metals Contamination**

The main concern of fly ash application in agriculture is the presence of heavy metals in FA. This waste contains many potentially toxic elements such as As, Cu, Zn, Cd, Pb, Co, Mo, Mn, Hg, Ni, Cr, Se, B, etc. [Pandey and Singh 2010]. The risk of pollution depends on the mobility of these elements. These heavy metals can be leached from soils, which contain particularly large amounts of FA, and can lead to pollution of land, groundwater, rivers and lakes. Many studies [Ram and Masto 2010, Singh et al. 2010, Pandey and Singh 2010, Ferreira et al. 2003] show that 5 to 30% of heavy metals present in FA are leachable. The most leachable elements are Cd, Cu and Pb. In addition, improperly conducted agricultural practices may affect the leaching of toxic elements from soils fortified with fly ash.

Unfortunately, there are still not many researches on the effects of FA on biological properties of soil. However, it is known that at higher concentrations of FA in soil, heavy metals may become more active and prevent microbial activity in the soil [Ram and Masto 2010]

For example, studies conducted in England [Tolle et al. 1983] indicate that some elements in high concentration are toxic to plants and animals. They point out that in plants grown in soils fertilized with FA, concentrations of elements such as B, Mo, As and Se were above the level considered toxic to animals and humans.

#### **Pollution with Radioactive Isotopes**

Fly ash also contains certain amounts of radioactive elements such as <sup>238</sup>U, <sup>232</sup>Th, <sup>40</sup>K, <sup>226</sup>Ra, <sup>210</sup>Pb, <sup>228</sup>Ra, <sup>222</sup>Ru i <sup>220</sup>Ru (radionuclides of uranium and thorium series). During the combustion process radioactive isotopes accumulate in the FA. Therefore, FA contains slightly elevated concentrations of these elements compare to the surrounding rocks and soils [Pandey and Singh 2010].

Studies conducted by Goyal et al. [Goyal et al. 2002] proved that in soil containing up to 24% FA, the activity levels of gamma emitting radionuclides such as <sup>40</sup>K, <sup>226</sup>Ra i <sup>228</sup>Ac, remained in permissible limits, despite local differences in the level of radiation. Also, ground water was not contaminated with radionuclides. However, due to the high harmfulness of these pollutants on living organisms, FA should be used in agriculture with caution.

### Soil Salinity

The application of fly ash (especially unweathered FA) as additive to soil can cause an increase of its salt content. Also, the salinity in the surrounding water reservoirs and ground water will increase. Salinity increases because of high concentration of totally dissolved solids, total hardness, cations and anions in FA leachates (mainly  $Ca^{2+}$ ,  $Na^+$ ,  $F^-$ ,  $CI^-$ ,  $SO_4^{2+}$ ,  $OH^-$  and  $CO_3^{2+}$  [Ram and Masto 2010].

The salinity increase can induce salt stress in plants. Different plant species respond in different way to salinity increase in soil. Plants can be classified, accordingly, as tolerant, moderately tolerant or moderately sensitive. The soluble ions can harm plants by direct toxic effects and also through significant changes in osmotic potential. For example, an elevated level of Na<sup>+</sup> reduces soil permeability, hydraulic conductivity, and infiltration by changing the soil structure. It also leads to erosion water logging, and surface runoff. High levels of inorganic and organic colloids can be released, which might transport contaminants such as pesticides, heavy metals and radionuclides [Sumner et al. 1998]. Therefore, crop productivity is decreasing with increasing salinity for most plants [Ferreira et al. 2003].

Although salinity and associated toxicity is a major limitation in the FA application in agriculture, the processes of FA weathering lead to significant reduction in a soluble salts concentration. Studies conducted by [Haynes 2009] showed that in FA after 3 years of weathering, the salt concentration dropped rapidly. In weathered FA the soluble salts concentration is no longer a limitation in its application in agriculture.

#### Long Term Effect of Fly Ash Application on Soil

Despite progress in the research, still little is known about the long-term effects of fly ash on soil. A universal method for the determination the leaching of toxic elements from fly ash is still missing, and most studies on this subject are based on industrial FA landfills rather than FA agricultural applications.

The similar situation applies to research connected with transport of soluble salts, heavy metals, radionuclides and other pollutants in soil fertilized with FA. As a result of interaction between FA and soil, pollutants behavior in FA – soil mixture, can vary considerably from their behavior in the pure FA.

Also, the processes of weathering of FA can have unpredictable effects on soil quality in the long term. These processes may lead to: changes in pH of the soil, decreases in Al and Si solubility through precipitation of non-crystalline aluminosilicates or clays with a low Al / Si molar ratio (storage of heavy metals), and production of secondary minerals (hydrated calcium silicate, hydrated calcium aluminosilicate, ettringite) in soil. As a result the porosity of the soil is reduced and its biological functions are disturbed [Ram and Masto 2010].

### CONCLUSIONS

Fly ash is a valuable secondary raw material, which is widely used in industry. A lot of research, including the one mentioned in this article, has indicated that FA can also be successfully used in agriculture.

FA can be used in agriculture, because it has unique physical and chemical properties. FA has a unique structure and contains almost all the nutrients necessary for proper plants growth and development. The application of FA in agriculture improves soil texture, reduces soil bulk density, improves water holding capacity, optimizes pH value, increases buffering capacity, increases soil aeration, percolation and water retention in the area of plant growth, reduces crush formation, provides macronutrients such as K , P, Ca, etc., provides micronutrients such as Fe, Zn, Cu, Mo, B, etc., reduces consumption of other additives (lime, fertilizers), reduces the mobility and availability

of heavy metals and has insecticidal properties as well [Pandey and Singh 2010]. It improves soil quality and increases yields. The amount and method of FA introduction into soil depends on its type, the type of crops, the prevailing climatic conditions, as well as the properties of FA.

Although FA utilization in agriculture has many advantages, there is a risk associated with its biological use. The main risk factor is that FA contains toxic elements (heavy metals, radioactive isotopes) and large amounts of dissolved salts. These substances can be leached from FA. Leaching can cause soil and water salinity, unfavorable changes in soil pH, increase of heavy metals mobility and availability and their accumulation in plants [Singh et al. 2010]. Therefore, caution must be taken with fly ash application in agriculture.

It is also important to continue and extend research concerning the effect of FA application in agriculture on crops and environment. Firstly, research should be carried out on the long-term impact of FA on soil properties, microbial activity and diversity as well as crops quality. Furthermore, the fate of toxic compounds contained in FA (including heavy metals and radionuclides) should be carefully investigated, both in the laboratory and field. Also, potential contaminants leaching from soil enriched with fly ash and their impact on the surrounding environment should be continuously monitored.

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#### REFERENCES

- 1. Ahmaruzzaman M., 2010: A review on the utilization of fly ash. Progress in Energy and Combustion Science 36, 327 363.
- Ajaz S., Tiyagi S., 2003: Effect of different concentrations of fly-ash on the growth of cucumber plant, Cucumis sativus. Archives of Agronomy and Soil Science 49, 457 – 461.
- 3. Ayala J., Blanco F., Garcia P., Rodriguez P., Sancho J., 1998: Austrian fly ash as a heavy metals removal material. Fuel 77 (11), 1147 1154.
- 4. Ciccu R., Ghiani M., Peretti R., Serci A., Zucca A., 2001: Heavy metal immobilization using fly ash in soils contaminated by mine activity. www.flyash.info/2001/mining1/06perett. pdf.
- Ciccu R., Ghiani M., Serci A., Fadda S., Peretti R., Zucca A., 2003: Heavy metal immobilization in the mining-contaminated soils using various industrial wastes. Minerals Engineering 16, 187 192.
- Ciećko Z., Żołnowski A. C., Kulmaczewska J., Chełstowski A., 2009: Effect of successive doses of drainage from coal ash to soil acidity (Wpływ następczy melioracyjnych dawek popiołów z węgla kamiennego na kwasowość gleby). Zeszyty problemowe postępów nauk rolniczych 535, 73 – 83.
- 7. Cornell R. M., Schwertmann U., 2003: The Iron Oxides: Structure, Properties, Reactions, Occurrences and Uses. Second ed. Wiley-VCH, Weinheim.
- 8. Eswaran A., Manivannan K., 2007: Effect of foliar application of lignite fly ash on the management of papaya leaf curl disease. Acta Horticulturae (ISHS) 740, 271–275.
- 9. Feng Y. J., Li F., Wang X. L., Liu X. M., Zhang L. N., 2006: Principal Chemical Properties of Artificial Soil Composed of Fly Ash and Furfural Residue. Pedosphere 16(5), 668-672.

- Ferreira C., Ribeiro A., Ottosen L., 2003: Possible applications for municipal solid waste fly ash. Journal of Hazardous Materials B96, 201 – 216.
- 11. Fulekar M. H., 1993: The pH effects on leachability of fly-ash heavy metals: laboratory experiment. Indian Journal of Environmental Protection 13, 185 192.
- Goyal D., Kaur K., Garg R., Vijayan V., Nanda S. K., Nioding A., Khanna S., Ramamurthy V., 2002: Industrial fly ash as a soil amendment agent for raising forestry plantations. In: Taylor P. R. (Ed.), 2002. EPD Congress and Fundamental of Advanced Materials for Energy Conversion, TMS Publication, Warrendale, PA, 251 – 260.
- Gracia G., Zabaleta I., Canibano J. G., Gyeyo M. A., 1995: Use of coal ash/mine waste in agriculture; their properties from griculture point of view. Coal Abstracts 95, 32 – 46.
- 14. Haynes R. J., 2009: Reclamation and revegetation of fly ash disposal sites -challenges and research needs. Journal of Environmental Management 90, 43 53.
- Iyer R.S., Scott J.A., 2001: Power station fly ash a review of value-added utilization outside of the construction industry. Resources, Conservation and Recycling 31, 217 – 228.
- 16. Kalra N., Joshi H. C., Chaudhary A., Chaudhary R., Sharma S. K., 1997: Impact of fly ash incorporation in soil on germination of crops. Bioresource Technology 61, 39 41.
- 17. Khan M. R., Khan M. W., 1996: The effect of fly-ash on plant growth and yield of tomato. Environmental Pollution 92, 105 – 111.
- **18.** Kumpiene J., Lagerkvist A., Maurice C., 2007: Stabilization of Pb and Cu contaminated soil using coal fly ash and peat. Environmental Pollution 145, 365 373.
- Lai K. M., Ye D. Y., Wong J. W. C., 1999: Enzyme activities in sandy soil amended with sewage sludge and coal fly ash. Water, Air, & Soil Pollution 113, 261 – 272.
- Mendki P. S., Maheshwari V. L., Kothari R. M., 2001: Fly-ash as a post-harvest preservative for five commonly utilized pulses. Crop Protection 20, 241 – 245.
- Menon M. P., Sajwan K. S., Ghuman G. S., James J., Chandra K., 1993: Fly ash-amended compost as a manure for agricultural crops. Journal of Environmental Science and Health, Part A: Environmental Science and Engineering 28, 2167 – 2182.
- **22.** Narayanasamy P., 2005: Prospect of use of fly-ash as a dust insecticide and a carrier in pesticide formulation. In: Proceedings of the National Seminar Cum Business Meet on Use of Fly-ash in Agriculture. FAUP, TIFAC, DST, New Delhi, 50 57.
- Narayanasamy P., Gnanakumar D., 1989: A. Lignite fly-ash: a nonpolluting substance for tackling pest problems. In: Devaraj KV (ed), 1989: Progress in pollution research. University of Agricultural Sciences, Bangalore, 201 – 206.
- Pandey V. C., Abhilash P.C., Singh N., 2009: The Indian perspective of utilizing fly ash in phytoremediation, phytomanagement and biomass production. Journal of Environmental Management 90, 2943 – 2958.
- **25. Pandey V. C., Singh N.,** 2010: Impact of fly ash incorporation in soil systems. Agriculture, Ecosystems and Environment 136, 16 27.
- Phung H. T., Lam H. V., Page A. L., Lund L. J., 1979: The practice of leaching boron and soluble salts from fly ash-amended soils. Water, Air, & Soil Pollution 12, 247 – 254.
- Ram L. C., Masto R. E., 2010: An appraisal of the potential use of fly ash for reclaiming coal mine spoil. Journal of Environmental Management 91, 603 – 617.
- **28. Riekerk H., 1984:** Coal-ash effects on fuel-wood production and runoff water quality. Southern Journal of Applied Forestry 8, 99 102.
- 29. Sankari S. A., Narayanasamy P., 2007: Bio-efficacy of fly-ash based herbal pesticides against pests of rice and vegetables. Current Science 92, 811 816.
- **30.** Singh A., Agrawal S. B., 2010: Response of mung bean cultivars to fly ash: Growth and yield. Ecotoxicology and Environmental Safety 73/ 8, 1950 1958.

- Singh R. P., A.K. Gupta, Ibrahim M. H., Mittal A. K., 2010: Coal fly ash utilization in agriculture: its potential benefits and risks. Review Environmental Science Biotechnology 9, 345 – 358.
- Sobik-Szołtysek J., Janecka B., 2006: Analysis of the possibilities of unconventional fly ash utilization (Analiza możliwości zagospodarowania popiołów lotnych metodami niekonwencjonalnymi). Ochrona Powietrza i Problemy Odpadów 40 (6), 184 – 193.
- 33. Sumner M. E., Miller W. P., Kookana R. S., Hazelton P., 1998: Sodicity, dispersion, and environmental quality, Sodic Soils: Distribution, Properties, Management and Environmental Consequences. In: Sumner M.E., Naidu R. (Eds.), 1998. Oxford University Press, New York, 149 – 172.
- 34. Szponder D. K., Trybalski K., 2009a: Identification of the fly ash properties by using different methods and equipments (Określanie właściwości popiołów lotnych przy użyciu różnych metod i urządzeń badawczych). Górnictwo i Geoinżynieria, 33/4, 287 298.
- 35. Szponder D. K., Trybalski K., 2009b: Influence of fly ash structure, phase and diversification of chemical composition on their utilization process. 13th Conference on Environment and mineral processing: 4.–6. 6. 2009, Ostrava, Czech Republic, Part I, VSB – Technical University of Ostrava, Faculty of Mining and Geology, Institut of Environmental Engineering; Ostrava, 121 – 127.
- Tolle D. A., Arthur M. F., Van Voris P., 1983: Microcosm/field comparison of trace element uptake in crops grown in fly ash amended soil. Science of the Total Environment 31, 243 263.
- 37. Vincini M., Carini F., Silva S., 1994: Use of alkaline fly ash as an amendment for swine manure. Bioresource Technology 49, 213 222.
- **38.** Właśniewski S., 2009: Effect of fertilization with fly ash from coal on selected chemical properties of sandy soil and yield of Atos (Wpływ nawożenia popiołem lotnym z węgla kamiennego na wybrane właściwości chemiczne gleby piaszczystej i plonowanie owsa). Ochrona Środowiska i Zasobów Naturalnych 41, 479 488.

# POPIOŁY LOTNE A ROLNICTWO – NOWOCZESNE ZASTOSOWANIA UBOCZNYCH PRODUKTÓW SPALANIA

Streszczenie. Pomimo ciągle rosnącego znaczenia alternatywnych źródeł energii, paliwa kopalne, w tym przede wszystkim węgiel kamienny i brunatny, odgrywają znaczącą rolę w globalnej gospodarce energetycznej. Niestety w procesach przetwarzania węgli na energię powstają uboczne produkty spalania, w tym popioły lotne. Odpady te w znaczący sposób oddziaływają negatywnie na środowisko naturalne, ale jednocześnie posiadają specyficzne właściwości umożliwiające ich wykorzystanie w przemyśle. Ze względu na bardzo duże ilość powstających popiołów lotnych, w ostatnich latach poszukuje się nowych, niekonwencjonalnych zastosowań dla tych odpadów. Ponieważ popioły lotne posiadają unikalną strukturę, a także zawierają w swoim składzie prawie wszystkie składniki odzywcze niezbędne dla prawidłowego wzrostu i rozwoju roślin, zwrócono uwagę na możliwość ich utylizacji w rolnictwie. Przede wszystkim stosuje się je jako substytut nawozu mineralnego do poprawy właściwości fizycznych, chemicznych i biologicznych gleb. Jednakże odpady te są również wykorzystywane jako środek zwiększający wzrost roślin i ilość otrzymywanych plonów. Ponadto, za pomocą popiołów lotnych zmniejsza się ilość metali ciężkich akumulowanych w roślinach czy też kontroluje rozprzestrzenianie chorób. Jednakże, ze stosowaniem popiołów lotnych w rolnictwie związane są pewne zagrożenia (m. in. skażenie gleb i wód powierzchniowych metalami ciężkimi i izotopami promieniotwórczymi, zasolenie gleb). Ponadto istnieje ryzyko związane z brakiem informacji na temat wpływu długotrwałego stosowania popiołów lotnych na jakość gleb i środowiska. W związku z tym celowe wydaje się podjęcie badań zmierzających do dokładnego określenia wpływu dodatku popiołów lotnych do gleb na produkcje rolniczą i środowisko naturalne.

W tej publikacji, autorzy podjęli się próby określenia właściwości popiołów lotnych umożliwiających i ograniczających wykorzystanie popiołów lotnych w rolnictwie. Przedstawili także nowoczesne zastosowania tych ubocznych produktów spalania w rolnictwie, a także ocenili korzyści i zagrożenia płynące z tego typu utylizacji.

Słowa kluczowe: popiół lotny, uboczne produkty spalania, rolnictwo, jakość gleb, nawożenie, zanieczyszczenie gleb.