UDC 662.613.125:63

P a r t 3

ASH AND SLAG HANDLING

3.5. Applications of ash and slag from power coals

3.5.4. Use of ash and slag for improving the properties of soil

3.5.4.2. Potential utilization of brown coal fly ash in agriculture

M. Gibczyńska, G. Hury, P. Kujawa, M. Romanowski
West Pomeranian University of Technology, Szczecin, Poland

ABSTRACT

Soil-introduced ashes affect mainly physical and chemical properties of soil, i.e. its reaction, acidity, amount of aluminium exchangeable, capacity of sorption complex and water absorbing power.

Addition of fly ash significantly enriched soil in exchangeable calcium and magnesium. During second and third year of the experiment it has been observed that the effect of brown coal ash presence tended to get lower.

Applied brown coal ash, despite using large quantities, did not contribute to abundance changes of metals: zinc, copper, nickel, lead and cobalt in soil and did not affect crop size, its structure and biometric features of cultivated plants.

1. GENERAL PROPERTIES OF BROWN COAL FLY ASH

World lignite coal deposits are to be found in a few countries, which include, apart from Poland, also Australia, China, the Czech Republic, Greece, Germany, Russia, the United States and Turkey. Extractable world lignite coal deposits are assessed at 512 milliard Mg**.** Poland is a country rich in extensive brown coal reserves. Polish indicated deposits are assessed at almost 14 milliards Mg, 58 milliards Mg contributing to prospecting deposits and estimated deposits constituting over 140 milliard Mg in coal-bearing areas [3]. In 2008 extraction of brown coal in Poland was 59,501 thousands Mg [4]. Production of electric power in Poland comes mainly from coal and its side effect is a large volume of furnace waste material such as fluidal ash, slag, ash and slag mixtures, ash from fluid bed boilers. Fly ash (artificial puzzolana) is produced during a process of pulverized coal combustion and exits ash furnace accompanied by flue gases. It is a fine-grain mineral powder, light-to-dark-grey and light-brown, consisting mainly of silicon, aluminium and iron oxides. Moreover, much the same as natural rock, it contains various trace elements and shows insignificant percentage of non-burnt coal parts. In general, ash consists of the following oxides: SiO_2, Al_2O_3, Fe_2O_3, CaO, MgO, Na_2O, K_2O and TiO_2. Ash contains also trace elements such as: Ba, Cu, Sr, Ni, Cr, Zn, Cd, Mo, V, Se, Pb, As and others. With respect to high contribution of ash components four component groups can be separated: basic components (SiO_2, Al_2O_3, Fe_2O_3, CaO), side components (MgO, SO_3, Na_2O, K_2O), trace components (TiO_2, P_2O_5, Mn and others) and non-burnt coal. Considering chemical composition fly ash is similar to volcanic ash. Glassy, often spherical particles have diameter 0.5…200 mm, and average size between 5 and 20 mm. Amorphous glassy form contributes to about 70…80 % of phasal composition of fly ash. Chemical composition of ash evidently depends on the type of combustion and coal. Generally, ash rich in silicon and aluminium oxides is produced from black coal while ash rich in calcium oxide from brown coal.

The most significant effect of coal composition on component content in ash is observed in case of coal combustion in conventional furnaces. According to current code of practice [5] three types of fluidal ash can be distinguished depending on the contribution of main components, i.e.: silicon, aluminium and calcium ash.

Brown coal ash does not contain large amounts of nickel, cadmium, arsenic and other elements, except for traces of nickel, cadmium, arsenic and other heavy metals; however, the ash is rich in calcium and magnesium [6]. According to British research papers fly ashes represent two classes: F and C. In F-class ash the amount of three most important oxides: silicon monoxide (SiO_2), iron oxide (Fe_2O_3) and aluminium oxide (Al_2O_3) exceeds 70 %, and percentage of CaO is less than 5 %. This type of ash is called low-calcium ash. In fluidal ash of class C the content of CaO is greater than 20 %, therefore it is called high-calcium ash [7]. Threshold waste material of these two types of power wastes are fly ashes from fluidal furnaces, containing not only regular waste material resulting from coal combustion, but also products of flue gas desulphurization [1]. Typical for this kind of ash is increased contents of calcium compounds, which in turn increases alkalinity. In Poland production of fly ash occurs mainly during coal combustion in heat and electric power stations. Annual output accounts for ca 13 million Mg. Use of ash as fertilizer in agriculture is the way of ash management produced during brown coal combustion., especially ash with increased content of calcium and magnesium. Ash introduced to soil affects most of all its physical and chemical properties like reaction, acidity, amount of aluminium absorbed by plants, capacity of sorption complex and water absorbing power. Fly ash directly applied to soil can be considered as calcium-magnesium fertilizer. Brown coal ash shows slightly weaker alkaline properties than basic calcium fertilizers; however it contains other components vital for plants, especially magnesium. This is an important fact because majority of arable land in Poland is magnesium deficient and over acidification.

Table 1**. Fly ash classification according to norm BN-79/6722-09 [5]**

Type of fly ash		Symbol	Contribution of basic components [%]			
			SiO_2	Al_2O_3	CaO	SO_3
1	Silicon ash	k	> 40	< 30	≤ 10	< 4
2	Aluminium ash	g	> 40	≥ 30	≤ 10	< 3
3	Calcium ash	w	> 30	< 30	> 10	≥ 3

2. EFFECT OF ASH ON PHYSICAL AND CHEMICAL PROPERTIES OF SOIL

2.1. Conditions of running a field experiment

The field experiment has been carried out on the area of Agricultural Experimental Station in Lipnik (near Stargard Szczeciński), on light soil (good rye complex) in the years 2004—2006. The research covered testing of seven fertilizer's variants (check control, oxide lime (CaO), dolomite lime $CaCO_3 \cdot MgCO_3$, ash from 1st electrofilter zone, from 2nd electrofilter zone, from 3rd electrofilter zone and mixture of ashes from three electrofilter zones). Calcium fertilizers and ashes have been applied in a dose corresponding to 1.0 hydrolytic soil acidity. Doses of each calcium fertilizer had been set considering the content of calcium and magnesium oxides. Brown coal ash produced by Power Plants ZE PAK S.A. Pątnów-Adamów-Konin contained on the average: 22.82 % of calcium, 3.62 % of magnesium, 0.07% sodium and 0.04% of potassium. Microcomponent content in ash fitted the limits respectively: zinc 18.2 – 26.4, copper 11.7 – 19.2, nickel 19.7 – 21.57 and cobalt 11.7 – 19.2 $mg \cdot kg^{-1}$ of ash. Ash used in the experiment did not contain lead. Reaction of applied fly ash determined as pH in H_2O varied from 11 to 13. In subsequent years of the field experiment spring crop triticale of Gabo and Wanad variety, spring rape and winter triticale were cultivated.

2.2. Reaction of soil

As a result of fertilization with ashes from three electrofilter zones and their mixture, soil has become alkaline (pH increased by ca half unit). Soil reaction changed due to high content of calcium and magnesium in ash. In most cases deacidifying effect of ash was similar to effect of oxide lime. In second and third year of the experiment tendency to reacidify has been observed, while check control soil did not show any variations.

2.3. Hydrolytic acidity

Soil acidity is strictly related to reaction of soil. Soil in field experiment where high-calcium brown coal fly ash was applied had typical hydrolytic acidity of 36.4 mmole $H^+ \cdot kg^{-1}$ of soil. In the first year of the experiment application of high-calcium ash decreased hydrolytic acidity of soil by ca 5.0 mmole $H^+ \cdot kg^{-1}$ of soil, i.e. by ca 20 %. During next year of the study hydrolytic acidity of soil fertilized by ash was again significantly lower. In the third year of study hydrolytic acidity of soil tended to drop, but by lower value compared to previous years. Obtained results prove stability of soil hydrolytic acidity.

2.4. Exchangeable aluminium

Toxic effect of exchangeable aluminium mainly affects root system of plants limiting its growth. Beneficial effect of liming relies in fact, on neutralization of exchangeable aluminium, bringing it to non-toxic limit or to decay in soil. In the discussed experiment where high-calcium fluidal ash of brown coal was applied, the content of mobile aluminium was 33.76 mg $Al \cdot kg^{-1}$ of soil in check control soil. Depending on electrofilter zone the impact of ash varied. Usage of ash from 1st and 3rd zone significantly decreased exchangeable aluminium content in soil (28.85 and 26.38 mg $Al \cdot kg^{-1}$ of soil, respectively). Fertilization with ash from 2nd zone or the ash mixture did not affect mobile aluminium content in soil. Aluminium content in the second year of the experiment remained at similar level as in the first year. In the last year of the experiment aluminium content in soil from all fields achieved the level typical for soil from check control field.

3. EFFECT OF ASH ON MACROCOMPONENT CONTENT IN SOIL

3.1. Exchangeable calcium and magnesium forms

Plants absorb calcium and magnesium in the form of ions from soil solution, thus abundance of exchangeable forms in soil is more important than general content of these elements. Calcium and magnesium are often considered merely as factors regulating soil reaction, their role in nutrition of plants being often neglected.

Soil in the experiment consisting in fluidal ash fertilization contained 434.98 mg $Ca \cdot kg^{-1}$ of soil of exchangeable calcium, and 24.46 mg $Mg \cdot kg^{-1}$ of soil of magnesium. Addition of fluidal ash with average contents of calcium 23 % and of magnesium 3.7 %, significantly enriched soil in exchangeable calcium and magnesium. Addition of ash from the 1st electrofilter zone resulted in high rise of exchangeable calcium (194.27 mg $Ca \cdot kg^{-1}$ of soil).

The highest amounts of exchangeable magnesium in soil were observed after application of ash mixture, and amounted correspondingly in subsequent years: 73.07, 46.71 and 43.49 mg $Mg \cdot kg^{-1}$ of soil. In successive years of the experiment the content of exchangeable calcium and magnesium dropped, although preserved at higher level than in check control soil. Thus usage of brown coal ash can become of special importance because a majority of arable lands in Poland is deficient in magnesium apart from its overacidification.

3.2. Available phosphorus and potassium

Standard liming as well as introducing ash rich in calcium is the main factor affecting the change of phosphate ion concentration in soil solution. Experimental soil contained in total 630 mg $P \cdot kg^{-1}$ of soil and 1225 mg $K \cdot kg^{-1}$ of soil; available forms of both elements contributing to ca 10 % of total content.

In the first year of the experiment check control soil contained 64.98 mg $P \cdot kg^{-1}$ of soil of available phosphorus. Due to fertilization of soil with high-calcium brown coal ash an important growth of available phosphorus in soil has been found. The greatest effect had been obtained after using ash from the 3rd electrofilter zone and ash mixture: the amount of phosphorus increased to 90.80 mg $P \cdot kg^{-1}$ of soil. In subsequent years of study available phosphorus in check control soil dropped down as well as in soil fertilized with ash.

However, during the three-years experiment the effect of ash entered to soil persisted.

Fertilization with high-calcium brown coal fly ash did not change available abundance of potassium in soil in a significant way. This observation may result from low amount of potassium in ashes produced during brown coal combustion.

3.3. Total and exchangeable iron

Apart from usual workout of iron resources in soil, very often iron becomes deficient due to reaction with phosphates or carbonates. In the discussed experiment total average content of iron in brown coal fluidal ash amounted to 26g·kg^{-1} of dry mass.

General content of iron in soil contributed to ca 0.6 %, which corresponds to average range for sandy cultivated land. Fly ash applied in the experiment of iron content up to 3 % had no significant effect on soil abundance of iron in total.

The content of exchangeable iron in soil varied from 777.99 to 804.91 mg Fe·kg^{-1} of soil. In the first and second year of the experiment fertilization with fly ash did not affect the amount of exchangeable iron in soil. In the last year of the experiment it was observed a significant increase of exchangeable iron in soil fertilized with ash from 1st and 2nd zone and in soil fertilized with ash mixture.

3.4. Exchangeable sodium

Based on the carried out studies it has been observed that application of high-calcium brown coal ash did not affect considerably the amount of exchangeable sodium in soil. Content of exchangeable sodium in each year was always similar to the content typical for sample soil.

4. EFFECT OF ASH ON MICROCOMPONENT CONTENT IN SOIL

4.1. Total manganese

Fluidal ash used to fertilize with manganese content for example amounting to 3000 mg Mn kg^{-1} of ash, can increase manganese abundance in soil. Soil from the experiment contained 299.7 mg Mn kg^{-1} of soil. Applied brown coal ash increased manganese content to the level of 325.5 mg Mn·kg^{-1} of soil, which resulted from ten times bigger content of manganese in ash compared to manganese abundance in experimental soil. After three years of the experiment content of total manganese again achieved the level typical for check control soil.

4.2. Zinc, copper, nickel, lead and cobalt

Applied calcium fertilizers both standard ones and brown coal ash, despite using large quantities, did not contribute to abundance changes of discussed metals: zinc, copper, nickel, lead and cobalt.

5. EFFECT OF COAL ASH ON THE CROP AND QUALITY OF PLANTS

In subsequent years of the discussed field experiment spring triticale and rape as well as winter triticale were cultivated. Soil fertilization with fluidal brown coal ash taken from three electrofilter zones did not affect crop size, its structure and biometric features of cultivated plants. Brown coal fly ash produced by Power Plants ZE PAK S.A. Pątnów–Adamów-Konin, used as soil fertilizer did not contribute to changes of general content of calcium, phosphorus and potassium in plant grain and seed. However, it should be emphasized that entering brown coal ash to soil significantly increased concentration of magnesium in grain of both varieties of spring triticale, due to changes occurring in experimental soil, because addition of fluidal ash of average contents of calcium 23 % and magnesium 3.7 %, enriched soil in exchangeable calcium and magnesium in substantial way [8, 2].

Application of high-calcium brown coal ash two vegetation seasons before only insignificantly worsened physical properties of grain; compared to grain from check control field winter triticale grain weight by volume considerably dropped down; moreover, contribution of the most ripe fraction, i.e. fraction of grain of diameter over 2.8 mm, diminished substantially [8].

6. PROSPECTS OF ASH MODIFICATION IN ORDER TO ADAPT TO FERTILIZATION NEEDS

Sludge used for agriculture purposes has to respond to specific requirements. One way is adding ash on next stage of sludge processing and using the mixture to plant fertilization. Obtained mixtures have low moisture while alkaline reaction of ash brings beneficial alkalinization of sludge. Also a process of sludge and ash composting is beneficial. Addition of brown coal ash to sludge slows down mineralization rate of organic substances contained in sludge thanks to which nitrogen and coal losses during composting of mixtures are smaller then loss in case of sludge without additions.

Fertilization based on high-calcium ash not only increases lime oxide and magnesium oxide content but also provides required amount of other plant nutrients. Ready-to-use fertilizer should form granulates. For a given granulate production thickening method needs to be simple in use, taking into account necessary equipment and processes of drying, storing, transport and loading. Transition from dusty material to granulate by means of appropriate adhesives places this product among multicomponent fertilizers, enabling creation of a special fertilizing composition. Such a process will determine future fertilizing sector in Poland. Therefore, fertilizer market for plants intended for biofuels and fuel biocomponents becomes potentially profitable niche [8].

REFERENCES

1. **Gawlicki M.,** Roszczynialski W. Nowe elementy w gospodarce odpadami energetycznymi. Mat. III Szkoły Gospodarki Odpadami, Rytro-Kraków. 2000.
2. **Gibczyńska M.,** Meller E., Hury G. Długotrwałość oddziaływania wysokowapniowego popiołu z węgla brunatnego na zawartość metali w glebie lekkiej. (The long durartion effect of ashes from brown coal on physical properties of light soil). Popioły z energetyki, Międzyzdroje, listopad 2007. 215-225.
3. **Libicki J.,** Tarasewicz Z. Projektowanie i budowa Kopalni Węgla Brunatnego "Legnica", Węgiel brunatny, 3, 2005, 1-5.
4. **Mały** Rocznik Statystyczny Polski GUS Warszawa 2008.
5. **Norma Branżowa - BN-79/6722-09** „Popioły lotne i żużle z kotłów opalanych węglem kamiennym i brunatnym; Podział, nazwy i określenia", 1976.
6. **Rosik-Dulewska Cz.** Podstawy gospodarki odpadami. Wydawnictwo Naukowe PWN Warszawa, 2002.
7. **Singh D.N,** Kolay P.K. Simulation of ash – water interaction and its influence on ash characteristics. Progress in Energy and Combustion Science 28, 2002. 267-299.
8. **Stankowski S.,** Pacewicz K., Gibczyńska M. Wpływ wapnowania gleby popiołem z węgla brunatnego na plon i jakość

ziarna odmian pszenżyta jarego. Przetwarzanie i wykorzystanie popiołów wysokowapniowych. Bełchatów, 22-24 lutego 2006r., 2006. 271-276.
9. **Świderska-Ostapiak M.** Popioły wysokowapniowe ze spalania węgla brunatnego jako półprodukt nawozów wapniowych i wieloskładnikowych. Popioły z energetyki, Międzyzdroje, listopad 2007. 227-235.