

2. ЕКОЛОГІЯ ДОВКІЛЛЯ

УДК 630*27

Д-р габ. М.А. Гібчинська¹; У.Б. Башуцька², канд. с.-г. наук;
Л.В. Лєвандовська¹

ВПЛИВ ЗОЛИ БУРОГО ВУГІЛЛЯ НА ФІЗИЧНІ ВЛАСТИВОСТІ ҐРУНТУ

Метою досліджень було визначення придатності висококальцевмісної золи після спалювання бурого вугілля на електростанції "Петнув-Адамув-Конін" для пониження кислотності мінеральних ґрунтів у західнопомеранських землях, а також вплив попелу порівняно із традиційними кальцієвими добривами – CaO та CaCO₃·MgCO₃. Предметом досліджень було визначення впливу золи після спалювання бурого вугілля на фізичні властивості ґрунту. Польовий експеримент здійснювали протягом трьох років (2004-2006 рр.) на легких ґрунтах. У перший рік експерименту вирощували ярі культури тритикале, другий – ярі культури ріпаку, третій – озимі культури тритикале. У зразках ґрунту визначали такі чинники: реакція, гідролітична кислотність, рухомий алюміній. Вже першого року після оброблення летким попелом із трьох зон електрофільтрів, а також попеловою сумішшю, збільшилась кислотність ґрунту стосовно контрольного зразка. Другого і третього років експерименту відзначено тенденцію вторинного окислення ґрунту. Відповідно висококальцевмісний леткий попіл з кожної зони електрофільтру та попелова суміш знижували гідролітичну кислотність кожного року досліджень.

Ключові слова: ґрунт, зола бурого вугілля, гідролітична кислотність, рухомий алюміній.

Dr. hab. M.A. Gibczyńska¹; U.B. Bashutska²; L.V. Lewandowska¹

Effect of brown coal ash on physical properties of soil

The aim of the carried out studies was estimation of suitability of high-calcium brown coal ash produced by Power Plants Pątnów-Adamów-Konin to deacidify mineral soil in West Pomerania lands, as well as of ash effect compared to traditional calcium fertilizers – CaO and CaCO₃·MgCO₃. The subject matter of studies was estimation of brown coal ash effect on physical properties of soil. Field experiment has been carried out in the years 2004-2006 on light soil. In the first year of the experiment spring crop triticale was grown, in the second – spring crop rape, and in the third – winter crop triticale. In soil samples the following factors have been determined: reaction, hydrolytic acidity, mobile aluminium. Already in the first year after treatment, fly ash from three electrofilter zones as well as ash mixture, increased pH of soil, compared to control soil sample. In the second and third year of the experiment it was observed a tendency to secondary acidification of soil. Due to applied high-calcium fly ash from each electrofilter zone and ash mixture, hydrolytic acidity dropped in each year of study.

Keywords: soil, brown coal ash, reaction, hydrolytic acidity, mobile aluminium

Introduction. Considering application of brown coal ash, the study mainly focused on biological land reclamation of post-industrial wastelands and on back-filling mine workings, road embankments and base courses. However, ash is a specific material good points of which should be competently used. Except for traces

¹ General Chemistry and Ecology Department, West Pomeranian University of Technology, Szczecin 71 434 Szczecin, ul Słowackiego 17,

² NUFWT of Ukraine, L'viv, O.Kobilyanskoyi st. 1, 79-005 Lviv, Ukraine (НЛТУ України, м. Львів)

of nickel, cadmium and arsenic, brown coal ash does not contain other heavy metals; instead, it is rich in calcium and magnesium (Rosik-Dulewska, 2002). In many countries research is carried out to apply ash in land cultivation. Studies conducted in South Africa revealed that fly ash can improve water capacity in excessively permeable soils (Kruger 2003). In Japan potassium and silicic fertilizer is produced with the use of fly ash.

According to the Ordinance of the Minister of Environment dated 27 September 2001 stating a list of wastes, combustion by-products (UPS), including brown coal ash produced by power plants, are non-hazardous wastes (Off. J. No 112, item 1206).

The aim of the carried out studies was evaluation of usefulness of brown coal ash produced by Power Plant Group Pątnów-Adamów-Konin to deacidify mineral soils on the area of West Pomerania and comparison of ash application with conventional calcium fertilizers CaO and $\text{CaCO}_3 \cdot \text{MgCO}_3$. The estimation of brown coal fly ash effect on physical properties of soil was the subject matter of the study.

Materials and methods. Conditions of running a field experiment. The field experiment has been carried out on the area of Agricultural Experimental Station in Lipnik (about 35 km south-east of Szczecin), on light soil (good rye complex) in the years 2004-2006. The experiment has been set up by means of randomized complete blocks. The area of each plot was 22 m². The research covered testing of seven fertilizer's variants (check control, burned lime (CaO), dolomite lime $\text{CaCO}_3 \cdot \text{MgCO}_3$, ash from 1st electrofilter zone, from 2nd electrofilter zone, from 3rd electrofilter zone and mixture of ashes from three electrofilter zones). Lime fertilizers and ashes have been applied in a dose corresponding to 1.0 hydrolytic soil acidity. Doses of each calcium fertilizer have been set considering the content of calcium and magnesium oxides. In the first year of the experiment spring crop triticale was cultivated, fertilized by P-17,5; K-50; S-6 kg/ha. Nitrogen fertilizer has been applied in the amount 90N kg/ha, (ammonium nitrate 34 % N),

In the second year spring rape was cultivated, NPK-fertilized which amounted to: N-130 (30 + 60 + 40); P-42; K-120; Mg-14; S-40 kg/ha. In the third year of the experiment winter crop triticale was cultivated. Prior to sowing the soil was fertilized with Polifoska Max (300 kg/ha), including: N-15; P-21; K-60; Mg-7,2; S-12 kg/ha, and 50 kg/ha of ammonium nitrate (34 % N) after triticale sowing. In spring, when vegetation started and at the moment of creating grass-blades, 68 and 51 kg N·ha⁻¹ of ammonium nitrate were applied.

Each year after harvesting, from each experimental plot combined soil samples have been collected at the depth 0-25 cm. Fertilizers' variants were the subject of the study. Analysis results of physical and chemical properties of soil were treated statistically by variance analysis whereas multiple comparison of average values was conducted by means of Tukey procedure assuming $\alpha=0,05$. Correlation coefficients have been calculated by means of Statistica 7.1 software.

Characteristics of brown coal ash

Average content of calcium and magnesium in high-calcium brown coal ash produced by Power Plants ZE PAK S.A. Pątnów-Adamów-Konin was dependent on electrofilter location zone. The highest content of both components was found in

the 3rd zone (Table 1). Potassium content in ash from each zone was similar (Table 1). Reaction of applied fly ash determined as pH in H₂O varied from 11 to 13.

Table 1. The content of calcium, magnesium and potassium in brown coal ash

Fraction of ash	Ca	Mg	K
	%		
Ash from I electrofilter zone	20,9	3,38	0,03
Ash from II electrofilter zone	23,0	3,61	0,04
Ash from III electrofilter zone	24,3	3,75	0,04
Mixture of ashes	23,1	3,75	0,04

Methods of soil analyses. Reaction of studied soil samples has been determined by potentiometers using extraction solutions: H₂O and KCL(PN-ISO 10390/1997). Soil hydrolytic acidity (Hh) has been determined using extraction by calcium acetate (II) (Krzywy et al., 1997). Mobile aluminium has been determined by Morgan method (Nowosielski, 1974).

Results and discussion. As a result of fertilizing with high-calcium brown coal fly ash produced by Power Plants ZE PAK S.A. Pątnów-Adamów-Konin light soils changed significantly their physical properties.

Reaction of soil

Table 2. The soil reaction (pH in H₂O, in KCl)

Fertilizing variants	pH in H ₂ O			pH in KCl		
	Years			Years		
	2004	2005	2006	2004	2005	2006
Control	6,27	6,22	6,29	5,06	5,41	5,40
CaCO ₃ ·MgCO ₃	6,51	6,37	6,26	5,57	5,35	5,17
CaO	6,99	6,88	6,76	6,30	6,18	6,12
Ash from I zone	6,84	6,75	6,54	6,28	6,14	6,06
Ash from II zone	6,46	6,52	6,68	5,89	5,51	5,84
Ash from III zone	6,85	6,79	6,72	6,19	6,18	6,26
Mixture of ashes	6,55	6,67	6,64	5,97	6,07	6,27
LSD _{0,05} I	0,258	0,231	0,132	0,320	0,219	0,390

n.s.d. – not significant difference

After harvesting spring crop triticale (2004), when compared to check control sample, pH in H₂O in soil fertilized with calcium fertilizers and ash was higher. Significant differences were noticed in soil fertilized with CaO, ash from 1st and 3rd electrofilter zones and ash mixture from all three zones (Table 2). In the first year of experiment due to application of calcium fertilizers, soil pH varied from 6.46 to 6.99. The highest value of pH in H₂O was observed in soil fertilized with calcium oxide (II). However, the effect of adding ash from 1st electrofilter zone of was the smallest. Such significant changes of soil reaction were caused – as it is well known – by presence of substantial amounts of calcium and magnesium included in ash. In the second and third year of experiment the soil tended to acidify again, while at the same time check control soil sample did not reveal any changes.

After applying KCl solution of concentration 1.0 mol · dm⁻³ to determine soil reaction in the first year of the experiment, the results obtained varied from 5.06 to

6.30 (Table 2). Similarly to data from other published studies, values of pH determined by using soil extraction with potassium chloride were lower than those determined as pH in H₂O. In the year 2004 in soil where calcium fertilizers were used, a significant rise of pH value was obtained, as compared to the data for the control soil. The lowest growth of pH in 1M KCl was obtained after fertilizing with dolomite (per every 0.51 unit), whereas other fertilizers increased value of pH much more (from 0.83 to 1.24 unit). The type of time-related changes and effect of applied calcium fertilizers was analogous to values obtained at determination of pH in H₂O.

The character of changes occurring in time and effect of applied calcium fertilizers was similar to values obtained when determining pH in H₂O and 1M KCl. Results of studies concerning time-related reaction changes of soil fertilized with high-calcium ash, confirm data given by Adamus (1976), who observed a return of soil reaction to initial level in two years after liming of light soil.

Hydrolytic acidity. In 2004, in non-fertilized soil, hydrolytic acidity was 3.64 cmolH⁺/kg of soil (Table 3). In the first year of the experiment liming decreased significantly hydrolytic acidity at a grower's soil humus level. The lowest value of hydrolytic acidity (2.77 cmolH⁺/kg of soil) was obtained after application of oxide lime, whereas application of high lime ashes and carbonate lime decreased hydrolytic acidity of soil in a similar way by ca 0.5 cmolH⁺/kg of soil, i.e. by ca 20 % (Table 3, Fig. 1). In the second year of the experiment (2005) hydrolytic acidity of soil from each plot where calcium fertilizers were applied was still much lower (Table 3, Fig.1). The smallest value of hydrolytic acidity amounting to 2.30 cmolH⁺/kg of soil, as in previous year, was determined in soil fertilized with CaO, and was significantly lower than its value in soil fertilized by CaCO₃·MgCO₃, 1st and 2nd electrofilter zones ash and ash mixture. In the third year of the experiment (2006) it has been noticed a tendency to further drop of hydrolytic acidity of soil; however, due to a serious decrease of hydrolytic acidity in control soil, relative drops were lower compared to preceding years. Results obtained from earlier studies proved stability of hydrolytic acidity of non-limed soil, whereas liming significantly decreased its hydrolytic acidity (Gibczyńska 2003).

Table 4. Hydrolytic acidity and mobile aluminium content in soil

Fertilizing variants	Hydrolytic acidity			Mobile aluminium		
	[cmol(+)/kg soil]			[mg Al/kg soil]		
	Years			Years		
	2004	2005	2006	2004	2005	2006
Control	3,64	3,50	2,77	33,76	30,00	33,87
CaCO ₃ ·MgCO ₃	3,14	2,96	2,70	28,07	29,37	32,42
CaO	2,77	2,30	2,17	26,66	25,88	30,89
Ash from I zone	2,94	2,80	2,50	28,85	30,00	34,33
Ash from II zone	3,18	2,85	2,35	35,70	30,60	31,42
Ash from III zone	2,92	2,59	2,37	26,38	26,88	33,53
Mixture of ashes	3,00	2,78	2,40	35,69	32,60	32,49
LSD _{0,05} I	0,415	0,336	0,204	3,39	n.s.d.	n.s.d.

n.s.d. – not significant difference

Mobile aluminium in soil

In the first year of experiment, in non-fertilized soil the content of mobile aluminium was 33.76 mg Al/kg of soil. Application of dolomite lime and oxide lime diminished significantly mobile aluminium content in soil (Table 4). Similar result has been obtained while applying 1st and 3rd zone ash. Fertilization of soil with 1st zone ash and ash mixture did not affect the content of mobile aluminium in soil in 2004. In the year 2005 aluminium content was similar to that in the first year. In 2006 aluminium content in soil from each plot reached the level of control sample.

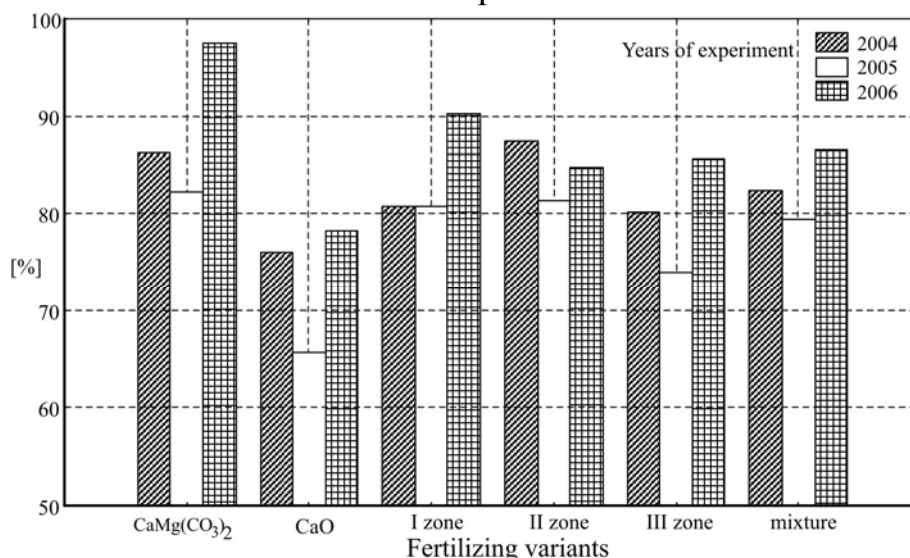


Fig. 1. Comparison of hydrolytic acidity of limed soil with control sample data taken as 100 %

Conclusions. Fertilization with high-calcium fly ash produced by combustion of brown coal in Power Plants Pątnów-Adamów-Konin changed significantly physical and chemical properties of light soil.

Already in the first year after treatment, fly ash from three electrofilter zones as well as ash mixture, increased pH of soil, as compared to the data from control soil sample. In majority of cases deacidifying effect of ash was similar to the effect made by application of oxide calcium.

In the second and third year of the experiment it was observed a tendency to secondary acidification of soil. Comparing the type of reaction changes in each year of the experiment a positive correlation has been found.

Due to applied high-calcium fly ash from each electrofilter zone and ash mixture, hydrolytic acidity dropped in each year of study. However, oxide lime affected changes of fertility indicator in this soil more than ash did.

Calcium fertilizers and brown coal fly ash applied to liming, in most cases decreased the content of mobile aluminium in soil in the first year of experiment, and in subsequent years they did not affect significantly its content.

References

1. Adamus M.: 1976. Effects of various liming rates on crop productivity and properties of light soil. In: Skutki wieloletniego stosowania nawozów. Sympozjum naukowe. Cz. II. Puławy, R (110), IUNG, Puławy: 131-138, (in Polish).
2. Głbczyńska M.: 2003. The effect of liming and crop rotation on hydrolytic acidity of light soil. Zesz. Nauk. AR Szczecin, 89: 95-102, (in Polish).

3. Kruger, R.A. 2003. Successful use of coal ash in South Africa. In. Mat. X Międzynarodowej Konferencji "Popioły z energetyki" W-wa 14-17 XI 2003, 53-70, (in Polish).
4. Krzywy, E., Nowak, W. & Wołoszyk, Cz. 1997. Agricultural chemistry. AR Szczecin, 18-26, (in Polish).
5. Nowosielski, O. 1974. Fertilization of vegetable plants. PWRiL Warszawa, 55, (in Polish).
6. Polish norm – PN-ISO 10390/1997, (in Polish).
7. Rosik-Dulewska, Cz. 2002. Basis of waste management. PWN Warszawa, 125, (in Polish).
8. The Ordinance of Minister Environment, 27.09. 2001, Off. J. No 112, item 1206, (in Polish).

УДК 332.64. *Доц. В.П. Оліферчук, канд. біол. наук; студ. М.Т. Матвієнко;
проф. І.Г. Войтович, канд. техн. наук – НЛТУ України, м. Львів*

МОЖЛИВІСТЬ ВИКОРИСТАННЯ ОСАДУ СТИЧНИХ ВОД ОЧИСНИХ СПОРУД ЛЬВОВА ДЛЯ ВИРОБНИЦТВА БІОГАЗУ

Здійснено експериментальні дослідження анаеробного перероблення мулу, який утворився після очищення стічних вод, в біогаз. Запропоновано встановити метантенки на каналізаційних очисних спорудах м. Львова. З'ясовано, що для використання осаду як добрива, треба вилучити важкі метали вже на стадії їх потрапляння в каналізацію. Тобто, треба заборонити скидати відходи з шкідливими домішками в міську каналізацію, а також контролювати всі підприємства, які не проводять очищення відходів виробництва.

Ключові слова: каналізаційні очисні споруди, мул, біогаз, ферментація.

*Assoc. prof. V.P. Olfierchuk; stud. M.T. Matvienko;
prof. I.G. Voytovich – NUFWT of Ukraine, L'viv*

Flow waters sediment use possibilities of Lviv's sewage disposal plant for biogas production

The experimental researches of silt anaerobic transformation what formed after sewage purification to biogas are made. It is suggested to set methanetanks on the Lviv's sewage disposal plant. It is set that for the use of sediment as fertilizer, it is needed to withdraw heavy metals already on the stage of their hit in the sewage system. That, it is needed to forbid to throw down wastes with harmful admixtures in the city sewage system, and also to control all enterprises which do not conduct cleaning of wastes of production.

Keywords: sewage disposal plant, silt, biogas, fermentation.

Стічні води міста Львова збираються та транспортуються через систему каналізаційних колекторів і насосних станцій на каналізаційні очисні споруди (КОС), де здійснюють їхнє механічне і біологічне очищення, після чого очищену воду скидають в річку Полтава, а густу фракцію вивозять на мулові майданчики.

Внаслідок очищення стічних вод утворюється багато осаду (мулу). Раніше весь оброблений осад транспортували для зневоднення і сушіння в природних умовах на мулові поля площею 20 га. Тепер у цеху механічного зневоднення мулу встановлено 7 центрифуг шведської фірми NOXON, які дадуть змогу вирішити одну з найскладніших проблем у системі водовідведення міста Львова – проблему зневоднення осаду стічних вод, який утворюється після біологічної очистки. У такому випадку на мулових майданчиках утворюється значно менше мулу, відповідно він займає менше місця. Та