UDC 621.9

Part 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

3.5.4.5. Effects of hard coal ash irrigation on release of chemical elements

T. Wojcieszczuk, E. Meller, A. Sammel, S. Stankowski, West Pomeranian University of Technology in Szczecin, Poland

ABSTRACT

Under laboratory conditions chemical composition of leachates from the soil fertilized with increasing doses of ash and chemical content of water passing through ash, ash+zeolite and ash+brown coal were determined. Additionally, chemical content of surface lysimeters water, the water passing through the profile as well as groundwater on the experimental object of power plant „Dolna Odra", were analysed. The amounts of chemical elements, soluble in water, from ashes of different origin were compared.

Chemical composition of leachates was affected by the origin of hard coal, the method of fertilising the surface layer of pile and the dose of ash applied as fertiliser.

INTRODUCTION

Ash, the residue of hard coal combustion for generating electricity, is not neutral to the environment irrespective of its management. Thus, analyzing chemical changes, both quantitative and qualitative, occurring in ash used as a soil fertilizer or stored in piles should be the basis for its utilization. Chemical weathering of minerals and also ash is considerably affected by water, which results in dissolving and displacement of chemical elements. In a relatively short time water alters the chemistry of introduced into the environment varying quantities of ash.

The aim of studies conducted by the Department of Soil Science was to determine the changes in some chemical properties of hard coal ash, incorporated into the environment, especially under the influence of water.

MATERIALS AND METHODS

The studies on soluble in water chemical elements of ash, by-product of hard coal combustion, were based on: laboratory experiments using the soil column for irrigated soils (PO nr 54427), the experimental object of "Dolna Odra" power plant where 4 lysimeters were used, and on the samples of ash collected from selected power plants.

The impact of ash fertilization on the amount of leached elements was examined on the soil material containing 12 % clay (<0,02 mm), 26 % silt (0,1…0,02 mm) taken from the layer 0…10 cm of brown-red soil. Ash from the power plant „Dolna Odra" was applied at the following doses: I – 0; II – 15; II – 60; IV – 120 t/ha. Soil columns were sprinkled once with 700cm^{-3} deionizer water.

Element migration from ash and ash supplemented with zeolite (clinoptiolite), brown coal was analyzed as follows: I - ash; II - ½ ash + ¼ zeolite + ¼ brown coal; III - ½ ash + ½ zeolite; IV – ½ ash + ½ brown coal.

In order to determine the chemical composition of surface water (S-1; S-2; S-3; S-4), (L-1; L-2; L-3; L-4), as well as groundwater (P-1; P-2; P-3; P-4; P-5; P-6), passing through ash, the experimental plot of „Dolna Odra" power plant and 4 lysimeters, each of which was 25 m^2 in area, were investigated. In 2002 lysimeters were filled with ash (0…170 cm), and the layer 0…40 cm of L-1 and L-2 was enriched with low peat (1 part of low peat +3 parts of ash), whereas L-3 and L-4 with the compost of coniferous tree bark, loose sand and fermented municipal sewage sludge.

The degree of ash components solubility was examined on composite samples collected from three objects: power plant „Burstyn" in Ukraine, power plant Vattenfall Heat Poland S.A. – former Elektrociepłownia Warszawa S.A. and power plant „Dolna Odra – Tama Pomorzańska" in Szczecin.

Chemical analysis of study material included determination of: *pH* in H_2O and *KCl* potentiometrically, (*S+Hh*) by the Kappen method, organic *C* by the Tiurin method, CO_3^{2-} by titrimetric method, Cl^- by argentometric method, Al^{3+} by the Sokolov method, macro- and microelements by ASA, total concentration of salts by conductometric method.

RESULTS

Introduced into the soil chemicals are leached downwards the soil profile with precipitation water and may also activate their natural resources. Therefore, before the utilization of various by-products as mineral fertilizers determining their chemical composition, especially the amount of easily soluble in water elements, is of a great importance.

Conducted studies show that the application of hard coal ash and soil irrigation results, first of all, in the change of soil reaction, also of the soil without ash fertilization. After 5 years, leachate reaction changed: in the soil without fertilization, from acid to slightly acid; in the soil with 15 and 60 $t \cdot ha^{-1}$ ash from slightly acid to neutral, and in the case of 120 t/ha ash from neutral to alkaline. At the same time, with the increase of applied dose of ash the amount of *Mg* and *Na* also increased [7]. Irrespective of ash dose, calcium turned out to leach first (*Tab. 1*) whereas the amount of *K*, *Mg* or *Na* depended on the applied dose of ash e.g. the highest amounts of *K* leached from the soil without fertilization and when the dose was 120 t/ha. At various *pH* values such elements as *Al, Fe, Mn* and *Zn* occurred in higher amounts in the leachate from the soil free of fertilization and after the application of 15 t/ha ash (*Tab. 1, 2*), [6,8].

Table 1. **Total sum of chemical compounds [mg/dm^3] leached from soil after 3 spray irrigations dependent on dose of ashes (expressed as mean values)**

Dose of ashes, t/ha	chemical composition							*pH*	Salinity, g*NaCl*/dm^3
	Ca	*K*	*Na*	*Mg*	*Cu*	*Al*	*Cl*		
0	497	160	56,3	41,5	0,042	2,4	53,5	5,0	1,93
15	460	139	60,8	69,7	0,046	2,3	45,2	5,4	1,86
60	507	123	20,6	130	0,056	ns*	46,1	6,3	2,36
120	572	148	155	184	0170	ns	50,6	7,2	3,30

*-ns – not observed

Table 2. **Total amount of leached elements after 12 sprinkling irrigations in mg/dm^3 (mean values)**

Dose of ashes, t/ha	*Zn*	*Mn*	*Fe*	*Cu*
0	2,64	5,19	0,53	0,12
15	0,59	1,33	1,16	0,20
60	0,20	0,15	0,65	0,22
120	0,15	0,18	0,60	0,26

Chemical components of ash not only differentiate soil nutrient resources but also change quantitative relationships between the pairs of elements, easily soluble in water. It was found, that depending on the applied dose of ash there are diverse relationships e.g. in the leachates of ash-free soil the highest value of correlation coefficient had K and Na (r_{xy}=0,95) and *Ca* and *Mg* (r_{xy}=0,94), [9, 12].

The amount of leached elements to a great extent depends on antagonistic and synergistic interactions between chemical elements, which is indirectly supported by the value of linear regression coefficient. With the increase of ash dose the amount of leached *Mg* was increasing in relation to the amount of *Ca*. Special attention should be paid to the value of regression coefficient between *Mg* and *K* cations .In the soil without ash fertilization leaching 1 g *Mg* was accompanied with 2.819g *K*. The value of regression coefficient was reduced after applying 15 t/ha ash but such a relationship was not observed at higher doses of ash (60 and 120 t/ha) (*Tab. 3*).

As a result of leaching the properties of ash fertilized soil changed (*Tab. 4*). Irrigation of topsoil (0…10 cm) brought about the increase in the concentration of hydrogen ions and depending on the ash dose the increase or decrease in some cations, easily soluble in HCl (concentration 0,1 mol/dm^3). Both in the soil with and without ash the increase in calcium ions was found whereas ash application resulted in the loss of *Mg, K, Na* [9].

Table 3 **Values of linear regression coefficient for chemical elements leached during sprinkling depending on a dose of ash, expressed in the same units. Only significant regression coefficients were considered**

Pair of chemical elements		dose of ash [t/ha]			
		0	15	60	120
x	y	by/x	by/x	by/x	by/x
Ca	*Mg*	0,074	0,137	0,256	0,334
Ca	*K*	0,201	0,147	0,099	0,092
Ca	*Na*	0,084	0,055	-	0,158
Ca	*Cl*	0,042	0,043	0,040	0,042
Mg	*K*	2,819	1,056	0,331	0,202
Mg	*Na*	1,200	0,384	-	-
Mg	*Cl*	0,640	0,302	0,128	-
K	*Na*	0,453	0,437	0,180	1,803
K	*Cl*	0,237	0,280	0,352	0,439
Na	*Cl*	0,507	0,339	1,421	0,232

Table 4. **Some chemical properties of soil (0-10 cm) depending on applied dose of ashes (expressed as mean values)**

Dose of ashes, t/ha	pH_{KCl}	*Hh*	*S*	increase (+) or decrease(-), (100 % free of sprinkling soil), %			
		0,1mol(+)/кg		*Ca*	*Mg*	*K*	*Na*
0	4,09	2,44	1,85	+13	+30	-46	-78
15	4,29	2,15	2,33	+21	-2	-44	-77
60	5,50	1,26	3,80	+41	-5	-40	-72
120	6,67	0,82	5,53	+55	-29	-42	-66

Coal ash deposited in piles transforms in its top layer (0…150 cm) into soil as a result of soil forming processes in which precipitation water is a factor whose impact on the chemical composition of ash may be investigated. Ash belongs to the materials which are easily permeable for precipitation water and therefore precipitation exerts influence on the direction of chemical changes in ash deposited in a pile.

Chemical changes are also affected by fertilizers used to accelerate sod formation on piles. Incorporating materials, rich in organic and chemical compounds from sewage sludge, into ash, on the one hand, facilitates plant growing and sodding but on the other hand, contributes to activating a considerable number of elements which are passing through the pile downwards with precipitation water. Experiments conducted on an experimental plot of „Dolna Odra" in Nowe Czarnowo revealed a distinct activation of larger amount of elements in more enriched ash. Even surface water from more fertilized lysimeters (S-3; S-4) contained more elements under study than the one from less fertilized lysimeters (S-1; S-2) (*Tab. 5*). Chemical content of lysimeters water percolating through ash and amendments is much more diversified. In less fertilized lysimeters (L-1; L-2) more Ca, K, and Na, passed downwards and in those more fertilized (L-2; L-4) more *Mg* and organic *C*, [10]. In addition, chemical composition of groundwater, within the experimental object, varied and depended on localization of piezometers as can be seen from the analysis of water samples in chosen piezometers (P-1, 2, 3, 6) (*Tab. 5*).

Ash obtained after hard coal combustion may be used for the reclamation of devastated areas instead of sand and gravel, which additionally protects other areas from devastation [4]. However, under the influence of precipitation they remain to be exposed to leaching process. This process is bound to slow down by amending sorbents such as humic acids and zeolite. The studies of references [1-3] depicted that both natural and synthetic zeolite are characterized by a considerable sorption capacity.

Laboratory experiment showed that ash and slag, brown coal and zeolite affected the amount of leached elements during spray irrigation depending on their content in particular variants. It was found that that the content of materials with sorption capacity had a significant influence on the amount of leached elements (*Tab. 6*). The leachate of the ash under investigation was characterized by high conductivity affected, first of all, by chlorides of magnesium and sodium. Among the applied sorbents, zeolite inhibited element leaching most whereas brown coal maintained high conductivity and enhanced calcium loss [11].

Table 5. **Content of chemical elements in surface water (S-1, 2, 3, 4) in lysimeters, in lysimeters water (L-1,2,3,4) and groundwater (P-1, 2, 3, 6) [mg/dm^3]**

Variant	Conductivity [mS/cm]	*Ca*	*Mg*	*K*	*Na*	organic *C*
S-1, S-2	0,12	12,0	1,33	12,6	6,0	2,23
S-3, S-4	0,15	13,9	1,65	13,8	4,5	6,69
L-1, L-2	1,67	247,7	37,4	141	129	2,02
L-3, L-4	4,68	53,0	806,6	97,5	80,2	4,13
P-1	0,44	39,1	7,1	17,2	34,7	4,13
P-2	1,26	86,1	32,5	56,9	151	5,31
P-3	1,44	126,6	35,1	36,7	140	2,98
P-6	0,65	108,5	23,8	1,9	9,6	16,0

Table 6. **Some chemical properties of leachates obtained after 3 sprinkling irrigations of ash with supplements under study placed in columns for irrigated soil studies (mean values)**

Variant (W)		Conductivity [mS/cm]	CO_3^{2-}	Cl^{1-}	*Ca*	*Mg*	*Na*	*K*
			[mg/dm^3]					
I		2,62	31,29	155,6	127,6	274	166	75,9
II		1,95	25,42	65,8	250,9	166	39	27,2
III		1,43	12,71	71,5	228,7	95	16	16,8
IV		2,28	28,36	72,6	307,3	224	105	25,3
$LSD_{0,05}$	W	0,24	5,51	4,24	34,0	30,0	18,1	12,9
	T	0,19	4,32	3,32	27,4	25,5	14,2	10,1
	W·T	0,49	11,11	8,54	70,8	60,5	36,0	26,0

I- ash; II - ½ ash, ¼ zeolite, ¼ brown coal; III - ½ ash, ½ zeolite; IV - ½ ash, ½ brown coal

Hard coal for electricity production comes from different deposits, has different origin and chemical composition and therefore there are differences in chemical content of ashes and solubility of particular elements in water.

Comparison of ash chemical content from three power plants „Burstyn" in the Ukraine, „Vattenfall" in Warszawa and „Dolna Odra - Tama Pomorzańska" in Szczecin demonstrated that quantitative differences concerning the content of easily soluble in water forms may be attributed to the total content of these forms [5]

The highest values for soluble *Ca, K* and *Na* were obtained from the ash from „Vattenfall", for *Mg* from „Burstyn" and „Dolna Odra - Tama Pomorzańska. The ash from „Dolna Odra - Tama Pomorzańska", contained a significantly highest amount of *Fe, Pb, Co* compared to other power plants (*Tab. 7*).

Ash incorporated into the soil, depending on its origin will affect the movement of particular elements into a soil solution in a specific way.

Table 7. **Average content of macroelements and microelements soluble in distilled water in ashes from hard coal combustion in selected power stations [mg/kg]**

Power Station	Ca		Mg		K		Na		Fe		Pb		Co	
„Bursztyn", the Ukraine	288	a*	37,4	a	14,4	a	7,50	a	0,023	a	0,048	a	0,021	a
„Vatenfall", Warszawa	6139	b	2,2	b	104,2	b	159,9	b	0,016	a	0,049	a	0,065	a
„Dolna Odra" Tama Pomorzańska Szczecin	77,7	c	36,4	a	6,4	a	3,37	a	0,145	b	0,146	b	0,128	b
NIR $_{0,05}$; LSD$_{0,05}$	217		11,8		11,66		5,78		0,11		0,065		0,059	

* - a, b, c - homogeneous groups

CONCLUSIONS

1. Ash amendments and irrigation change chemical properties of fertilised soil due to macro- and microelement leaching resulting in soil acidity, total bases decrease and increasing value of hydrolytic acidity.
2. The changes in chemical properties of the soil fertilised with growing doses of ash as a result of irrigation are demonstrated by the gain or loss of cations under study. The higher the ash dose the higher the amount of Ca remained in the soil whereas the content of K and Na was reduced.
3. Irrigation and chemical elements leaching, change quantity relationships depending on the ash dose, which is supported by calculated regression coefficients. This relationship refers, first of all, to the ratio Ca:Mg and Ca:K.
4. Surface lysimeter water running off contains chemical elements from ash and amendments and their amount is much higher in the water percolating through lysimeters downwards into groundwater. On investigated experimental plot the chemistry of groundwater depended on the location of piezometer, hence different chemical content.
5. Brown coal and zeolite, used to reduce leaching of chemical elements from ash, had a different impact on the quality and quantity of absorbed elements. Zeolite amendment lowered the amount of Mg, Na and K in leachates and brown coal increased the amount of calcium.
6. Chemical content of leachates is also affected by the origin of hard coal from which ash was obtained, especially in the case of Ca, Mg and K cations.

REFERENCES

1. **Brogowski Z., Dobrzański B., Kocon J.,** Zaniewska-Chlipalska E. 1983. The possibility of zeolite occurrence In the soil of Poland. Zesz. Probl. Post. Nauk Rol. 220: 489-493.
2. **Gworek B.** 1993. Wpływ zeolitów na zmniejszenie akumulacji metali ciężkich w roślinach uprawianych na glebach zanieczyszczonych. Rozp. Nauk. SGGW W-wa.
3. **Gworek B., Borowiak M., Kwapisz J.** 1998. Effect of zeolite-bearing rocks upon inactivation of cadmium In soil. Rocz. Gleb. 49, ½: 71-78.
4. **Maciak F., Liwski S., Prończuk J.** 1976. Rekultywacja składowisk odpadów paleniskowych (popiołów) z węgla brunatnego. Rocz. Gleb. 27, 4: 149-185.
5. **Wojcieszczuk T., Meller E., Sammel A., Stankowski S.** 2009. Zawartość i rozpuszczalność niektórych składników chemicznych w popiołach o różnym pochodzeniu. Zesz. Probl. Post. Nauk Rol. 535: 483-493.
6. **Wojcieszczuk T., Niedźwiecki E., Meller E.,** 1996. Zmiany w składzie chemicznym gleby i uzyskiwanych z niej przesączów pod wpływem zróżnicowanego nawożenia popiołem z Elektrowni „Dolna Odra". Rocz. Gleb. 47, ¾: 213-221.
7. **Wojcieszczuk T., Niedźwiecki E., Meller E.,** 2001. Zawartość wapnia, magnezu i sodu w przesączach glebowych w zależności od zastosowanej dawki popiołu. Biul. Magnezol. 6, 3: 405-410.
8. **Wojcieszczuk T., Niedźwiecki E., Meller E.,** 2003. Zawartość Fe, Mn, Cu, Zn w przesączach glebowych po zastosowaniu popiołu z węgla kamiennego. Zesz. Probl. Post. Nauk Rol. 493: 515-520.
9. **Wojcieszczuk T., Niedźwiecki E., Meller E.,** 2004. Wpływ nawadniania i popiołu z węgla kamiennego na właściwości chemiczne gleby lekkiej. Rocz. Gleb. 55, 1: 249-255.
10. **Wojcieszczuk T., Niedźwiecki E., Sammel A.,** Maciorowski R. 2007. Skład chemiczny wód, roślin i użyźnionego popiołu w badaniach lizymetrycznych na obiekcie doświadczalnym Elektrowni „Dolna Odra". Zesz. Probl. Post. Nauk Rol. 518: 203-208.
11. **Wojcieszczuk T., Niedźwiecki E., Sammel A.,** Wojcieszczuk M. 2007. Składniki chemiczne w przesączach po deszczowaniu popiołu z węgla kamiennego oraz popiołu z dodatkiem zeolitu lub węgla brunatnego. Zesz. Probl. Post. Nauk Rol. 520: 417-423.
12. **Wojcieszczuk T., Niedźwiecki E., Sowińska M.** 2007. Współzależność występowania składników chemicznych w przesączach z gleby nawożonej zróżnicowanymi dawkami popiołu z węgla kamiennego. Journal of Elementology. 9, 4: 847-855.

T. Wojcieszczuk, E. Meller, A. Sammel, S. Stankowski. Effects of hard coal ash irrigation on release of chemical elements // Proceedings of the IV scientific and practical workshop “Ashes from TPPs: removal, transport, processing, landfilling”, Moscow, April 19–20, 2012 — M.: MPEI-Publishers, 2012. P. 204 – 207.