ECOLOGICAL CHEMISTRY AND ENGINEERING A

Vol. 18, No. 9–10 2011

Stanisław KOWALIK[1] and Jerzy WÓJCIK[1]

ANALYSIS OF CHEMICAL PROPERTIES OF THE INCINERATION WASTES AND THE POSSIBILITIES OF THEIR BIOLOGICAL RECLAMATION

ANALIZA WŁAŚCIWOŚCI CHEMICZNYCH ODPADÓW PALENISKOWYCH POD KĄTEM ICH BIOLOGICZNEJ REKULTYWACJI

Abstract: The paper presents the results of the studies of chemical properties of the incineration wastes, 8 years after finishing their deposition in the sedimentation pond using the method of hydraulic transportation. The studies referred to 5 horizons of the profile up to the depth of 80 cm and 3 zones systematically distant from the place of the wastes deposition.
The results indicate that within 8 years there was a displacement of a significant amount of components to the deeper layers of the profile, and consequently the decrease in pH and electrolytic conductivity. However, the satisfactory effect such as diminishing the pH value to the level tolerable for the majority of higher plants refers only to layer 0–10 cm in the whole study area and 0–20 cm in the area up to 400 m from the point of discharge. The properties of wastes after 8 years from their deposition in the sedimentation pond do not allow efficient biological reclamation of the object without applying remediation measures.

Keywords: incineration wastes, chemical properties, reclamation

In Poland, the development of coal-based energy industry causes that a large amount of incineration wastes are disposed on the heaps and in sedimentation ponds, the area of which is over 3000 ha [1]. These objects, after finishing their construction, should be immediately subdued to reclamation measures. The most important task is carrying out measures allowing quick introduction of vegetation that would permanently secure the repository from eolic erosion (harmful to the neighbouring areas) and stimulate soil-making processes, and consequently, make the area productive [2–5]. For this purpose,

[1] Department of Environmental Management and Protection, AGH University of Science and Technology in Krakow, al. A. Mickiewicza 30, 30–059 Kraków, Poland, phone: +48 12 617 22 43, email: skowal@agh.edu.pl, jwojcik@agh.edu.pl

different techniques and technologies are applied, such as isolating the surface of the sedimentation pond with soil formations, or the improvement of the properties and enrichment of the ash mass with wastewater sludge [2, 4, 6–8]. Because of technological reasons it sometimes happens that such objects are temporarily not covered by reclamation measures and, despite initially extremely unfavourable chemical properties, after some years the process of their covering with vegetation starts during spontaneous succession [1].

This paper presents the results of studies referring to the chosen chemical properties of incineration wastes in the vertical section of the sedimentation pond and dimension of the sedimentation pond, in terms of their biological reclamation, 8 years after the end of their deposition.

Material and methods

The studies were carried out on the sedimentation pond of the incineration wastes "Czajki II", made in the process of the combustion of hard coal in the cogeneration plant of the Nitrogen Industry Plant *Zakłady Azotowe* (Z.A.) Tarnow-Moscice. This sedimentation pond was located in the hole after gravel exploitation, where initially lime was deposited, and after removing the lime the pond was filled with incineration wastes, which had been hydrotransported there.

The results of the studies carried out in the first year after ending the deposition of wastes on the mentioned above sedimentation pond and some other sedimentation ponds of the cogeneration plant in Moscice, showed clear spatial differentiation of their properties. The grain composition usually corresponded to dust or clay formations with 20–30 % content of colloid silt. They were characterized by low proper and volume density (2.0–2.15 $g \cdot cm^{-3}$ and 0.8–1.2 $g \cdot cm^{-3}$, respectively) and about 50 % general porosity. They showed strongly alkaline reaction (pH 8.8–10.1) and elevated electrolytic conductivity (about 0.9 $mS \cdot cm^{-1}$) [1, 3].

In the studies carried out 8 years from finishing the deposition, chemical properties were analysed in the wastes taken from 5 layers (0–10 cm; 10–20 cm; 20–40 cm; 40–60 cm and 60–80 cm), in three zones of distance from the place of their discharge (250–300 m, 350–400 m and 450–500 m). The samples of the material were analysed with standard laboratory methods. There were the following analyses: pH, electrolytic conductivity (formation: water as 1:5), roasting losses, total N (Kjeldahl method), elements Ca, Mg, K, Na, Fe, P, Zn, Cu, Sr, Pb and Cd extracted in mixture of $HClO_4$ and HNO_3 acids in 4:1 proportion using the AAS method and ions extracted in H_2O: Ca^{2+}, Mg^{2+}, K^+ and Na^+ – using the AAS method, SO_4^{2-} (using the Polish standard PN-79 C-04566), Cl^- (using the PN-ISO 9297) and HCO_3^- (using the PN 90/C 04540/3). To find the statistic significance of the differences in the basic properties of wastes, between the subsequent layers in the vertical section of the sedimentation pond, the assessment of the homogeneity of variance was made by the Levene's test, and then by one-factor analysis of variance and LSD ($\alpha = 0.05$).

Results and discussion

Sedimentation ponds for incineration wastes are objects that are difficult to reclaim biologically, because of some unfavourable physical and chemical properties, first of all strong alkaline reaction of the disposed material. Such formations, despite great general porosity (about 50 %) do not show good aeration, due to the small amount of macropores and small proper density, with a great participation of the dust fraction, which makes them susceptible to eolic erosion [9, 10]. Hydraulic transport and discharge point of a semiliquid mass causes its segregation and significant spatial differentiation of both physical and chemical properties. The carried out studies during first 3 years after ending the deposition of wastes on several ash sedimentation ponds in Z.A. Tarnow, referring to their chemical properties and spontaneous succession of vegetation, indicate that there is a process of the transfer of the components into the profile and slow diminishing of the pH, especially in the surface horizons and subsequent entering of mosses and vascular vegetation tolerating alkaline reaction [1, 3].

The results of the studies carried out 8 years after the end of the waste deposition indicate significant differentiation of the analysed chemical properties both in the profile up to the depth of 80 cm, as well as in space, proportionally to the distance from the point of their hydraulic discharge. The greatest changes occurred in the surface layer of the sedimentation pond, of 10 cm thickness, in which pH of the material was 7.8 and was 0.9 units lower than the reaction recorded 3 years after finishing the construction of the repository [1]. In the vertical section up to the depth of 60 cm there was a growing trend of the pH value, and then its stabilization on the level of 8.8 (Table 1). The differences in pH values of layers 0–10 cm and 10–20 cm were statistically significant (LSD test), as well as between these layers and deeper layers (20–80 cm).

Table 1

Basic chemical properties of incineration wastes 8 years after finishing their deposition in the sedimentation pond

Layer [cm]	Statistical parameter	pH in H_2O	Electrolytic conductivity (EC) [$mS \cdot cm^{-1}$]	$CaCO_3$	Roasting losses in 400 °C
				[%]	
0–10	Mean SD	7.77 0.15	0.193 0.033	1.20 0.37	9.01 1.90
10–20	Mean SD	8.33 0.31	0.212 0.110	2.25 0.82	5.93 3.51
20–40	Mean SD	8.60 0.30	0.356 0.208	1.77 0.25	5.29 1.87
40–60	Mean SD	8.83 0.08	0.517 0.168	1.55 0.53	3.75 0.53
60–80	Mean SD	8.80 0.20	0.491 0.185	1.53 0.29	6.23 4.56
LSD ($\alpha = 0.05$, n = 6)		0.25	0.144	n.s.	2.85

Mean – Arithmetic mean; SD – Standard deviation; n.s. – not significant differences.

In layer 0–10 cm of the whole sedimentation pond, within 8 years there was a change of reaction from strongly alkaline into slightly alkaline, also in the layers 10–20 cm in the zone up to 400 m from the point of discharge and 20–40 cm, in the zone up to 300 m the value of pH did not exceed 8.5. So it can be regarded that the reaction of the wastes is currently tolerated by many plant species. Compared with the initial state, pH lowered in the whole analysed vertical section, the most in the surface layer (0–10 cm), on aver-

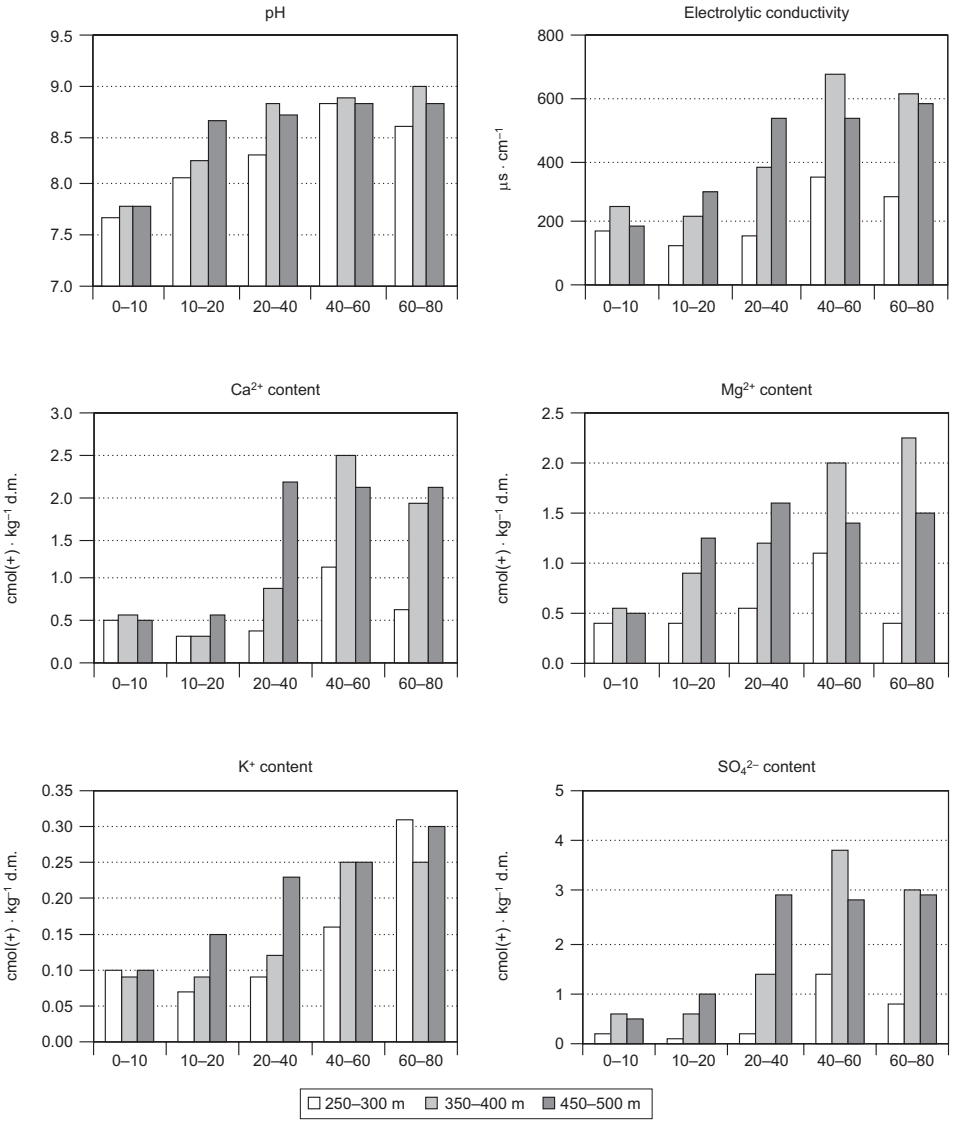

Fig. 1. The formation of selected properties of incineration 8 years after ending their deposition in the sedimentation pond, depending on the distance from the discharge point (water extract)

age more than 1 unit, the smallest decrease was on the depth of 40–80 cm – less than 0.5 unit. A differentiation of this property was also stated in the connection with the distance from the point of the hydraulic discharge of wastes, while the smallest decrease, only 0.3 unit refers to 0–10 cm layer (SD = 0.15), the largest – above 1 unit was found on the depths of 10–20 cm (SD = 0.31) and 20–40 cm (SD = 0.30). The value of pH usually grows with the distance from the point of discharge (Fig. 1).

A similar distribution refers to the values of electrolytic conductivity. The lowest was found in the layer 0–10 cm – 0.19 mS · cm^{-1}, with a clearly growing trend down to the depth of the vertical section to 60 cm (the difference between layers 0–10 cm and 10–20 cm from one side and deeper layers from another, was statistically significant). With the growing distance from the point of discharge of wastes it was found that the growth of the value of the electrolytic conductivity in upper layers to the depth of 60 cm (Fig. 1).

The growth trend down the depth of the vertical section was also in case of all the ions analysed in the water's extract (Table 2). The increase of the contents of K^+ and Na^+ with the depth took place in the whole examined vertical section of the decantation pond, while in the case of the content of Ca^{2+}, Mg^{2+} and SO_4^{2-} the growing trend ended on the depth of 60 cm. This indicates that sodium and potassium moves deeper than other analysed ions, which, in large amount, are stopped on the depth of 40–60 cm. The contents of these ions in the vertical section, counted in chemically equivalent units, are many times larger than the contents of K^+ and Na^+. This explains the described distribution of pH and electrolytic conductivity values in the formations of the studied layers, as well as the confirmed during the fieldwork phenomenon of their cementation on the depth of 40–60 cm, also noticed by some authors [1, 6, 10]. It can also be stated that with the growth of the distance from the point waste discharge the content of the ions analysed in water solution grew, however it can be undoubtedly applied only to the range of depth 10–40 cm (Fig. 1).

Table 2

The content of selected ions in water extract in the incineration wastes 8 years after finishing their deposition in the sedimentation pond

Layer [cm]	Na^+	Mg^{2+}	K^+	Ca^{2+}	SO_4^{2-}	Cl^-	HCO_3^-
	[cmol(+) · kg^{-1} d.m.]						
0–10	0.10	0.50	0.10	0.52	0.39	0.09	0.80
10–20	0.09	0.85	0.10	0.43	0.54	0.09	1.00
20–40	0.11	1.12	0.15	1.15	1.50	0.14	1.13
40–60	0.16	1.49	0.19	1.91	2.71	0.08	1.20
60–80	0.22	1.37	0.29	1.55	2.23	0.10	1.20

In other analysed properties similar regularities were not found. The content of $CaCO_3$ is shaped on a close level in the whole profile (1.2 do 2.25 %) slightly higher content was recorded only in horizon 10–20 cm. The losses of roasting are medium for the particular layers in the range 3.75–9.01 %, however they show large differentiation

(depending on the horizon V = 21 to 59 %). The largest values were found in horizon 0–10 cm, at relatively low variability (V = 21 %), while the largest differentiations occurred in horizon 10–20 cm (V = 59 %). A similar distribution can be found in the case of total content of N and P in the vertical section of the sedimentation pond (Tables 1 and 3).

Table 3

The total content of macroelements in the incineration wastes 8 years after finishing their deposition in the sedimentation pond

Layer [cm]	Na	Mg	K	Ca	Fe	P	N
	[g · kg^{-1} d.m.]						
0–10	2.88	7.14	5.87	16.09	23.18	2.12	1.09
10–20	2.26	10.40	5.77	18.09	45.10	1.92	0.57
20–40	1.98	8.57	3.90	16.81	35.88	1.45	0.37
40–60	2.38	7.76	4.47	13.04	25.14	1.29	0.32
60–80	2.35	7.77	4.03	14.63	33.71	1.24	0.76

The total content of other macroelements, despite clear differentiation in the profile, do not show clear trends of changes (Table 3). The largest mean content of Ca and Mg was found in layer 10–20 cm, while N, P, K and Na – in a layer 0–10 cm. The differentiation of contents of these components in the connection with the distance from the point of waste discharge is considerable, however only in the case of Ca and Mg in horizons 10–20 cm and 20–40 cm one can state clear growing trend with the distance (Fig. 2).

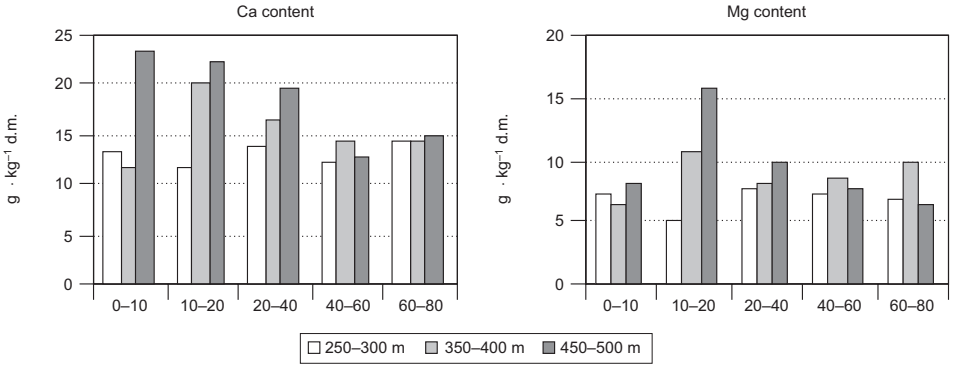

Fig. 2. The formation of general contents of selected elements in the incineration wastes 8 years after ending their deposition in the sedimentation pond, depending on the distance from the discharge point

The results of the determinations of total contents of alkaline elements and their content in the water solution show that their removal resulted in lowering pH and the electric conductivity; this mainly refers to the layers up to 40 cm.

Tabela 4

The total content of selected trace elements in the incineration wastes 8 years after finishing their deposition in the sedimentation pond

Layer [cm]	Cu	Zn	Sr	Cd	Pb
	[mg · kg^{-1} d.m.]				
0–10	61.50	45.70	61.17	0.31	39.83
10–20	61.33	41.33	48.73	0.25	25.33
20–40	48.33	41.37	38.07	0.23	33.33
40–60	51.17	51.00	37.57	0.32	39.17
60–80	50.00	55.10	34.83	0.33	40.50

The results of the determinations of total contents of trace elements do not show clear trend of the differentiation in the vertical section of the sedimentation pond (Table 4). It can also be stated that the contents of these elements do not exceed threshold values for arable and forest land, defined by the Enactment of the Minister of Environment "referring to the standards of the quality of soil and the quality of ground" (Dz.U. nr 134, poz. 1140).

Conclusions

1. Within the period of 8 years from ending the deposition of incineration of wastes in the sedimentation pond there was a displacement of a significant amount of the components down the deeper layers of the profile, and as a result of this process pH values and the values of electrolytic conductivity of wastes decreased.

2. A sufficient effect such as the decrease of pH values of wastes to the level tolerable by most of plants occurred in layer 0–10 cm in the whole area and in layers 10–20 cm in the zone up to 400 m from the point of discharge and 20–30 cm in the zone up to 300 m.

3. The total contents of macroelements, despite clear differentiation in the vertical section of the sedimentation pond, do not show clear trends of changes. The highest contents of N, P, K and Na were found in the layer of 0–10 cm, while Ca and Mg in the layer of 10–20 cm. With the increase of the distance from the point of wastes disposal, only in case of the content of Ca and Mg in layers 10–20 cm and 20–40 cm; there was a growing trend.

4. The contents of trace elements do not show clear trend of differentiation in the vertical section of the sedimentation pond and stay within the limits defined as acceptable in the standards for soils on arable and forest land.

5. The properties of the incineration wastes after 8 years from their deposition in the sedimentation pond still do not allow efficient biological reclamation of the object without applying remediation measures.

References

[1] Tymińska-Zawora K., Krzaklewski W., Kowalik S. and Wójcik J.: Inż. Środow. 2003, **8**(1), 15–27.
[2] Antonkiewicz J.: Ecol. Chem. Eng. 2005, **12**(3), 209–215.

[3] Krzaklewski W., Kowalik S. and Wójcik J.: [in:] International Symposium on the Reclamation, Treatment and Utilization of Coal Mining Wastes. VSB-Technical University, Ostrawa 1996, p. 157–161.
[4] Rogalski M., Kardyńska S., Wieczorek A., Poleszczuk G. and Śmietana P.: Zesz. Probl. Post. Nauk Roln. 2001, **477**, 255–259.
[5] Wysocki W.: Sozologia i Sozotechnika 1988, **26**, 231–240.
[6] Kowalik S., Wójcik J. and Tymińska-Zawora K.: Inż. Środow. 2001, **6**(1), 183–194.
[7] Wong J.W.C. and Su D.C.: Bioresource Technol. 1997, **59**(2–3), 97–102.
[8] Strzyszcz Z.: Ocena przydatności i zasady stosowania różnorodnych odpadów do rekultywacji zwałowisk oraz terenów zdegradowanych działalnością przemysłową. IPIŚ PAN, Zabrze 2004, 82 p.
[9] Bogacz A., Chodak T. and Szerszeń L.: Zesz. Probl. Post. Nauk Roln. 1995, **418**, 671–676.
[10] Gilewska M.: Roczn. Glebozn. 2004, **55**(2), 103–110.

ANALIZA WŁAŚCIWOŚCI CHEMICZNYCH ODPADÓW PALENISKOWYCH POD KĄTEM ICH BIOLOGICZNEJ REKULTYWACJI

Katedra Kształtowania i Ochrony Środowiska
Akademia Górniczo-Hutnicza w Krakowie

Abstrakt: W pracy zamieszczono wyniki badań właściwości chemicznych odpadów paleniskowych po 8 latach od zakończenia ich składowania w osadniku metodą hydrotransportu. Badania dotyczyły 5 warstw w przekroju pionowym osadnika do głębokości 80 cm i 3 stref systematycznie oddalonych od miejsca zrzutu odpadów.

Uzyskane wyniki wskazują, że w okresie 8 lat nastąpiło przemieszczenie znacznej ilości składników do głębszych warstw osadnika i w konsekwencji zmniejszenie wartości pH i przewodności elektrolitycznej. Jednak wystarczający efekt w postaci zmniejszenia wartości pH do poziomu tolerowanego przez większość roślin wyższych dotyczy tylko warstwy 0–10 cm na całej badanej powierzchni i 0–20 cm w strefie do 400 m od punktu zrzutu. Właściwości odpadów po 8 latach od ich zdeponowania na osadniku nie pozwalają na efektywną rekultywację biologiczną obiektu bez zastosowania zabiegów naprawczych.

Słowa kluczowe: odpady paleniskowe, właściwości chemiczne, rekultywacja