



## Effect of mechanical activation of fly ashes on selected pollutants removal from landfill leachates

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Received 24 September 2014; Accepted 3 March 2015

### ABSTRACT

Fly ashes can be considered to be good pollutants adsorbents because of their physico-chemical properties, among others, well expanded surface area and C-S-H phase. Thanks to them fly ashes are able to absorb and immobilize pollutants present in landfill leachates. The surface area of fly ashes can be enlarged by mechanical activation. Larger surface area predisposes fly ashes to bound high quantities of pollutants from various media. The aim of the present research work was to evaluate the effect of mechanical activation on the ability of two fly ashes (from lignite and coal burning) to immobilize selected pollutants present in landfill leachates. Composition of leachates was typical for mature dumping places with TOC values reaching  $355 \text{ mgC L}^{-1}$  and ammonium nitrogen up to  $230 \text{ mgN-NH}_4^+ \text{ L}^{-1}$ . Heavy metals concentration was in the range of  $<0.1\text{--}0.3$  (Cd) and  $1.1\text{--}2.0$  (Zn)  $\text{mg/L}$ . Mechanical activation was performed in a special activator at temperature  $21^\circ\text{C}$  for 15 min. Mechanical activation transpired effective in the case of fly ashes from coal burning. The permeability coefficient of these fly ashes changed compared to nonactivated ash (the control sample), from  $1.54 \times 10^{-5}$  to  $5.46 \times 10^{-6} \text{ m/s}$ . Organic pollutants, measured as TOC, were immobilized in over 14% better than in the case of not activated ash. Over 17% improvement of ammonium nitrogen removal from leachates by activated ashes was also stated compared to the control sample. Activation of fly ashes from brown coal burning did not show any significant impact on immobilization properties.

*Keywords:* Fly ash; Mechanical activation; Landfill leachates; Ammonium nitrogen; Heavy metals; Adsorption

### 1. Introduction

Municipal waste storage in landfills is inseparably connected with the generation of leachates. The

composition of leachates depends, among others, on climatic factors, properties of the wastes which are dumped in landfill and the water balance in the layer of wastes [1]. The volume of leachates is affected by the initial moisture of dumped wastes, physical, chemical and biological processes which take place in

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landfill and by inflow of water from outside of landfill (e.g. rainfall) [1]. Leachates contain high concentrations of both organic and inorganic pollutants; exemplary characteristics of them are given in Table 1. The composition of leachates varies a lot depending not only on the factors described above but also on the maturity of the waste layer [2]. Because of high pollution, leachates cannot be allowed to discharge directly into the environment. They must undergo treatment, which nowadays usually combine techniques involving chemical, physical and biological processes [3]. Some of processes used in landfill leachate treatment, e.g. membrane processes and biological processes, require this wastewater to be pretreated. Many pretreatment techniques may be used including adsorption [3]. Adsorption is used mainly for removal of recalcitrant compounds from landfill leachates. It can be realized by filtering leachates by granulated activated carbon columns [3]. Despite advantages of this technique (e.g. a large surface area of activated carbon, inherent physical properties), it is economically not effective. A promising alternative to activated carbon could be fly ashes. Fly ashes are a part of hearth wastes generated during coal or lignite burning. The ashes are caught in the dust equipment. They have both ion exchange and adsorption properties [4,5]. The chemical composition of exemplary fly ashes is given in Table 2. Values of the permeability coefficient for fly ashes are usually at the level of  $10^{-4}$ – $10^{-6}$  cm/s [6,7]. This range of permeability is roughly equivalent to the range of permeability of silty sand to silty clay soil [7]. Ashes having fine grains have a lower value

Table 1  
Landfill leachates characteristics from various landfill places [2]

Parameter	Range
pH	4.5–9
Total solids, mg L <sup>-1</sup>	2,000–60,000
TOC, mg L <sup>-1</sup>	30–29,000
BOD <sub>5</sub> /COD <sub>Cr</sub>	0.02–0.8
COD <sub>Cr</sub> , mgO <sub>2</sub> L <sup>-1</sup>	140–152,000
BOD <sub>5</sub> , mgO <sub>2</sub> L <sup>-1</sup>	20–57,000
Organic N, mgN L <sup>-1</sup>	14–2,500
Ammonium N, mgN-NH <sub>4</sub> <sup>+</sup> L <sup>-1</sup>	50–2,200
Total phosphorus, mgP L <sup>-1</sup>	0.1–23
Chlorides, mgCl <sup>-</sup> L <sup>-1</sup>	150–4,500
Sulphates, mgSO <sub>4</sub> <sup>2-</sup> L <sup>-1</sup>	8–7,750
Heavy metals (total of Cd, Cr, Cu, Pb, Hg, Ni, Zn), mg L <sup>-1</sup>	0.07–1,029.66 (with the most abundant Zn, followed by Cu. The less abundant Hg followed by Cd)

Table 2  
Chemical composition of fly ashes from 49 power plants in USA [7]

Property	Fly ashes, % by mass
CaO	0.37–27.68
SiO <sub>2</sub>	27.88–59.40
Al <sub>2</sub> O <sub>3</sub>	5.23–33.99
Fe <sub>2</sub> O <sub>3</sub>	1.21–29.63
MgO	0.42–8.79
SO <sub>3</sub>	0.04–4.71
Na <sub>2</sub> O	0.20–6.90
K <sub>2</sub> O	0.64–6.68
TiO <sub>2</sub>	0.24–1.73
LOI (loss of ignition)	0.21–28.37

of the permeability coefficient [7]. Taking into consideration the fact that over 90% of electric and heat energy in Poland derives from fossil fuels burning, the amount of fly ashes generated in power plants is huge. Around 4 mln tones of fly ashes are generated in Poland annually [8]. About 84.4% of them are recovered; 14.7% are treated; almost 0.9% are temporarily stored [8]. It means that at least 0.04 million tones of fly ashes, a year could be used in industry and environmental protection.

They are also much cheaper than activated carbon and because of this they can be used for treating liquid wastes including landfill leachates. Fly ashes are considered to be a good material for removal of organic compounds (COD), heavy metals and NH<sub>4</sub><sup>+</sup> from landfill leachates [4,9]. Studies by Xue et al. indicated that in bath tests with a dose of fly ash equal to 10 g/L and leachate of pH 9 (reaction time 60 min), the removal rate of heavy metals was as follows: Zn 39.42%, Pb 59.24%, Cr 28.14%, Cd 55.37% and Cu 32.82% [10]. R. Devi and R.P. Dahiya showed that on fly ash almost 88% of COD was captured provided that wastewater of the initial COD equal to 1,080 mg/L was used. Also, in this case, bath experiments were conducted and the dose of fly ash was equal to 60 g/L (reaction time 250 min.) [11]. Ammonium removal efficiency by zeolitized fly ash was about 40% (adsorption capacity equal to 0.4 mgN-NH<sub>4</sub><sup>+</sup>/g of adsorbent) [12]. However, activated fly ashes were able to remove 44–94% of ammonium nitrogen from landfill leachates. The most effective activation method was sodium hydroxide calcinations–hydrothermal treatment [13].

Capacity of fly ashes for immobilization of pollutants present in leachates can be increased by their chemical or mechanical activation. Mechanical activation causes some structural defects in fly ash granules and increases their surface area. A larger surface area allows for more affective immobilization of pollutants

in fly ashes because reactivity of activated ashes is greater [14,15]. Until now, mechanical activation has been mainly used for modification of properties of sorbents used in desulphurization of exhaust fumes. Mechanical activation allowed for a decrease in the quantity of sorbents used in desulphurization of about 20% [16]. Research works on the effects of mechanical activation on immobilization properties of fly ashes towards pollutants present in landfill leachates are of great interest, and our approach to the problem—activation of ashes to increase their immobilization potential for the pollutants from leachates—is innovative.

The aim of the investigation was to evaluate the effect of mechanical activation on ability of fly ashes for immobilization of some pollutants present in landfill leachates.

## 2. Materials and methods

### 2.1. Characteristics of fly ashes and leachates

Random samples of fly ashes collected from Jaworzno and Turów power plants were used in the study. Jaworzno power plant burns coal. It is a power plant complex in southern Poland which has a total capacity of 1,435 MWe (from five units of 225 MWe and one unit of 220 MWe). It is one of the largest and state-of-the-art electric power plants in Poland. Turów power plant burns lignite. At present, it is the most high electric power plant in Poland. At present, it has a total capacity of 1,498.8 MWe. The important difference between coal and lignite is that they have different values of the calorific value. As a result to generate the same quantity of electric power 2.5 more of lignite must be burned compared to coal. Burning of lignite generates, however, only half of the amount of ash obtained during coal burning.

Leachates were obtained from Sobuczyna municipal landfill place. It is a dumping place located close to Częstochowa city (southern Poland). Characteristics of fly ashes and landfill leachates used during experiment are presented in Tables 3 and 4.

The composition of the fly ashes (Table 3) used in the study was within the range obtained by other

authors [2] for fly ashes. Fly ashes from lignite burning contained significantly lower percentage shares of  $Mn_2O_3$  and  $P_2O_5$  than those from the Jaworzno power plant. They also contained almost 90% less  $Na_2O$  than fly ashes from coal burning. Fly ashes from the Turów power plant were, however, richer in CaO (both total and free).

As can be seen from the results given in Table 4, leachates from the Sobuczyna landfill place are characteristic for mature landfills, with relatively low TOC and relatively high ammonium nitrogen concentration of pH of leachates was alkaline. It contained also average concentrations of sulphides and chlorides and not very high (compared to other leachates) concentrations of heavy metals [2]. The most abundant heavy metal was zinc (concentration range 1.1–2.0 mg/L), the less abundant one was cadmium (concentration in the range <0.1–0.3 mg/L). Because of low original concentrations of heavy metals in leachates, they were enriched with heavy metal salts (zinc sulphate, cuprum chloride, nickel sulphate and cadmium sulphate) to obtain the concentration of about 10 mg/L of each metal.

In present research work, we have focused only on selected pollutants immobilization by fly ashes. They were

Table 4  
Selected physicochemical properties of leachates from Częstochowa municipal landfill

Parameter	Range
pH	8.4–8.9
Alkalinity (to phenolphthalein), mval L <sup>-1</sup>	1.0–4.8
Alkalinity (to methyl orange), mval L <sup>-1</sup>	16.9–38.0
Total hardness, mval L <sup>-1</sup>	11.1–18.2
Chlorides, mg L <sup>-1</sup>	615–1,210
Sulphates, mg L <sup>-1</sup>	375–455
Ammonium nitrogen, mg L <sup>-1</sup>	166–199
TOC, mg L <sup>-1</sup>	169–345
Zn, mg L <sup>-1</sup>	1.1–2.0
Cu, mg L <sup>-1</sup>	0.36–0.65
Ni, mg L <sup>-1</sup>	<0.1–0.48
Cd, mg L <sup>-1</sup>	<0.1–0.3

Table 3  
Composition of fly ashes used in the study, %

Power plant	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO total	CaO free	MgO	Mn <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	Na <sub>2</sub> O
Jaworzno	44.0	32.0	4.2	0.3	4.5	0.1	0.6	0.7	5.2
Turów	43.9	33.5	11.4	2.1	1.4	0.007	0.4	0.1	0.6

- (1) organic compounds (measured as TOC) because in leachates from old landfill places they are present as nonbiodegradable compounds and cannot be treated with biological methods,
- (2) ammonium nitrogen—which at high pH value is toxic for living micro-organisms,
- (3) chlorides—they are well soluble compounds which cause salinity of water, and it is difficult to remove them by biological methods,
- (4) heavy metals—toxic inorganic compounds, which are not removed in biological processes and can cumulate in sludge and other types of sediments.

## 2.2. Mechanical activation of fly ashes

To evaluate the possibilities of fly ash properties modification, the ashes taken from Jaworzno and Turów power plants were mechanically activated. Mechanical activation is a physical process which does not involve chemical reagents. A mechanical activator (Fig. 1) was used for this purpose.

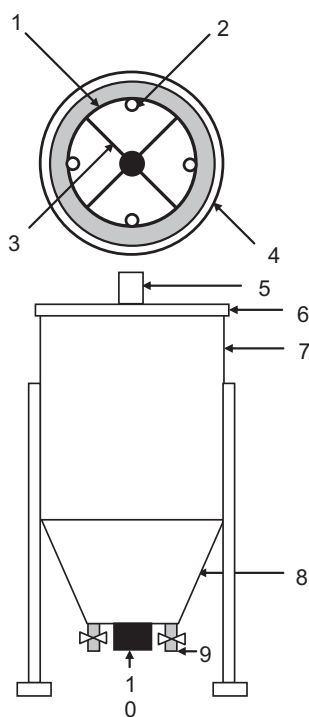


Fig. 1. Scheme of a mechanical activator used for activation of fly ashes from Jaworzno and Turów power plants: 1—coat of rotor, 2—tap hole of activated material, 3—vane of rotor, 4—housing, 5—inlet, 6—cover, 7—activation chamber, 8—chamber to collect activated material, 9—stub pipes with valves, 10—motor [15].

Shoulders of the activator rotor driver with electric engine collided with ash grains and caused superficial defects (spot and linear) in the ash structure. Activation of fly ashes was performed under air-dried conditions, at ambient temperature of 21 °C. In all 3 kg of each fly, ash was activated. Fly ash was introduced into an activator partially through inlet. Mechanical activation lasted for 15 min.

## 2.3. Immobilization flow experiment

Experiment was conducted under flow conditions using lysimetric columns. Lysimetric columns were PVC tubes with internal diameter of 10.5 cm. Activated fly ashes were mixed with distilled water at ratio 2:1 (w/w). Lysimeters were filled with the mixture of ash and water. To fill the column, 800 g of ash and 400 mL of water were used. After 21 days, the mixture solidified. The control sample (containing not mechanically activated fly ash/water mixture) was running simultaneously. Then, the columns were flooded 6 times with landfill leachates (respectively samples I, II, III, IV, V, and VI). The volume of leachates which can be pour into lysimetric column was calculated based on volume of solidified ash–water mixture. Volume of the mixture was for each column multiplied by porosity value for the ash. Based on this product, one-time exchange of poured landfill leachate was estimated. During the research work, the estimated value was doubled in order to achieve appropriate quantities of the material for analyses.

Samples for analysis of solidified ash–water mixture the permeability coefficient were also prepared. The permeability coefficient was measured with a variable gradient method. The permeability coefficient was calculated according to the following equation:

$$k = \frac{a}{t} \left[ -\ln \left( 1 - \frac{s}{h} \right) \right], \text{ m s}^{-1}$$

where  $k$ —permeability coefficient,  $\text{m s}^{-1}$ ;  $a$ —height of sample, m;  $h$ —initial water table height, m;  $s$ —water table decrease in time, m;  $t$ —time of leachate flow, s.

## 2.4. Physicochemical characteristics of leachates

In raw leachate and in leakage, the following physicochemical properties were measured:

- (1) pH potentiometrically,
- (2) alkalinity (by titration method),
- (3) total hardness with titration method using EDTA,

- (4) chlorides by argentometric titration,
- (5) ammonium nitrogen—with Nessler method,
- (6) TOC by infrared analysis using the MultiN/C Analytik Jena analyzer.

Analyses were conducted in triplicate according to Standard methods [17].

The total content of selected heavy metals ions (Zn, Cu, Cd, Ni, Pb) in leachate was analysed in unfiltered samples after concentrated HNO<sub>3</sub> and HCl (1 + 3—aqua regia) digestion. The content of metal ions was detected by an atomic absorption spectrometry method, using an AAS spectrometer Carl Zeiss, Germany.

### 3. Results and discussion

Selected physicochemical properties of leakage from columns with not mechanically treated fly ashes (control sample) and mechanically activated for Jaworzno and Turów power plants are listed in Tables 5–8.

As can be seen leakages from all columns packed with activated and not activated fly ashes had alkaline pH. Compared to the pH of not treated landfill leachate, pH value increased. The remaining parameters decreased. The highest decrease was observed in the case of TOC and ammonium nitrogen. The initial concentration of TOC was up to 355 mgC L<sup>-1</sup>. In leakages, it did not exceed 224 mgC L<sup>-1</sup>. Ammonium nitrogen concentration in landfill leachate was in the range 160–230 mgN-NH<sub>4</sub><sup>+</sup> L<sup>-1</sup>. In the leakages from Jaworzno, PP ashes concentration of ammonium nitrogen did not exceed 132 mgN-NH<sub>4</sub><sup>+</sup> L<sup>-1</sup> (in leakages from the columns filled with activated ash/water mixture did not

Table 5

Physicochemical properties of leakage from lysimetric columns filled with not mechanically activated ash–water mixture from Jaworzno power plant

Parameter	I	II	III	IV	V	VI
pH	9.3	9.2	9.2	9.1	9.2	9.3
Zp, mval L <sup>-1</sup>	5.0	3.1	3.0	2.8	3.2	3.5
Zm, mval L <sup>-1</sup>	16.1	11.9	11.0	9.8	12.3	13.6
T, mval L <sup>-1</sup>	13.0	13.6	14.0	11.2	12.8	13.8
Cl <sup>-</sup> , mg L <sup>-1</sup>	650	672	688	1,080	1,110	1,200
N-NH <sub>4</sub> <sup>+</sup> , mg L <sup>-1</sup>	120.0	132.0	114.0	118.8	108.0	112.8
TOC, mg L <sup>-1</sup>	69.0	113.2	92.5	224.0	108.2	131.0
Zn, mg L <sup>-1</sup>	0.2	<0.1	0.1	<0.1	0.1	0.2
Cu, mg L <sup>-1</sup>	<0.1	<0.1	0.1	0.2	0.3	0.2
Ni, mg L <sup>-1</sup>	0.1	<0.1	<0.1	<0.1	<0.1	0.2
Cd, mg L <sup>-1</sup>	<0.1	<0.1	<0.1	<0.1	0.15	0.1

Table 6

Physicochemical properties of leakage from lysimetric columns filled with mechanically activated ash–water mixture from Jaworzno power plant

Parameter	I	II	III	IV	V	VI
pH	9.3	9.3	9.1	9.2	9.4	9.3
Zp, mval L <sup>-1</sup>	3.5	3.3	2.1	3.1	4.2	4.0
Zm, mval L <sup>-1</sup>	16.1	16.5	13.8	18.9	24.0	27.6
T, mval L <sup>-1</sup>	13.2	12.0	13.4	12.0	13.6	14.8
Cl <sup>-</sup> , mg L <sup>-1</sup>	606	670	680	1,008	1,238	1,228
N-NH <sub>4</sub> <sup>+</sup> , mg L <sup>-1</sup>	81.9	96.2	86.9	72.9	95.0	82.2
TOC, mg L <sup>-1</sup>	55.0	94.6	64.0	112.8	65.8	134
Zn, mg L <sup>-1</sup>	<0.1	<0.1	0.1	<0.1	<0.1	0.1
Cu, mg L <sup>-1</sup>	<0.1	<0.1	<0.1	<0.1	0.1	0.15
Ni, mg L <sup>-1</sup>	<0.1	<0.1	<0.1	<0.1	0.1	0.1
Cd, mg L <sup>-1</sup>	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1

Table 7

Physicochemical properties of leakage from lysimetric columns filled with not mechanically activated ash–water mixture from Turów power plant

Parameter	I	II	III	IV	V	VI
pH	9.3	8.7	8.8	9.3	9.3	9.3
Zp, mval L <sup>-1</sup>	1.9	0.9	1.0	3.0	3.8	4.8
Zm, mval L <sup>-1</sup>	6.1	7.2	10.3	18.5	25.5	29.4
T, mval L <sup>-1</sup>	55.7	43.0	26.3	14.3	16.5	16.3
Cl <sup>-</sup> , mg L <sup>-1</sup>	689.0	497.0	204.0	116.0	38.0	19.5
N-NH <sub>4</sub> <sup>+</sup> , mg L <sup>-1</sup>	129.0	129.5	120.0	118.5	133.5	132.5
TOC, mg L <sup>-1</sup>	103.3	199.8	241.0	51.2	71.5	127.0
Zn, mg L <sup>-1</sup>	0.3	0.15	0.1	0.1	0.2	0.3
Cu, mg L <sup>-1</sup>	0.1	0.2	0.1	0.15	0.1	0.2
Ni, mg L <sup>-1</sup>	0.2	0.1	0.1	0.1	0.1	0.3
Cd, mg L <sup>-1</sup>	<0.1	<0.1	<0.1	<0.1	0.15	0.1

Table 8

Physicochemical properties of leakage from lysimetric columns filled with mechanically activated ash–water mixture from Turów power plant

Parameter	I	II	III	IV	V	VI
pH	9.6	9.0	8.6	9.1	9.3	9.2
Zp, mval L <sup>-1</sup>	2.2	1.0	0.9	2.1	5.2	5.2
Zm, mval L <sup>-1</sup>	4.4	5.8	9.3	18.4	27.8	30.3
T, mval L <sup>-1</sup>	47.8	39.3	29.6	17.6	17.2	16.9
Cl <sup>-</sup> , mg L <sup>-1</sup>	675.0	377.5	266.0	78.0	30.0	23.0
N-NH <sub>4</sub> <sup>+</sup> , mg L <sup>-1</sup>	117.0	128.5	139.0	116.0	130.5	131.0
TOC, mg L <sup>-1</sup>	47.3	349.3	213.6	79.8	89.7	146.9
Zn, mg L <sup>-1</sup>	0.1	0.1	0.1	0.2	0.15	0.2
Cu, mg L <sup>-1</sup>	<0.1	<0.1	<0.1	0.1	0.1	0.1
Ni, mg L <sup>-1</sup>	<0.1	0.1	0.2	0.15	0.1	0.1
Cd, mg L <sup>-1</sup>	<0.1	<0.1	<0.1	<0.1	0.1	0.1

exceed 95 mgN-NH<sub>4</sub><sup>+</sup> L<sup>-1</sup>). In the leakages from Turów PP, it did not exceed 132.5 and 139 mgN-NH<sub>4</sub><sup>+</sup> L<sup>-1</sup>, for the control and activated ash sample, respectively. Concentrations of chlorides in leakages from Jaworzono PP were comparable to the observed in landfill leachate before treatment procedure. The analysis of chlorides concentrations in leakages indicates that during the experiment a disadvantageous phenomenon concerning washout of chlorides in amounts exceeding the concentrations present in leachate inflow took place. Unlike the ashes from Jaworzono PP, the ones from Turów PP caught high quantities of chlorides. Their concentrations in leakages (I–VI) decreased systematically both in mechanically activated and control samples. Concentrations of heavy metals in leakages from not activated ashes were at the level of 0.3 and less mg/L. The most abundant compound was zinc, and the less abundant was cadmium, which was similar to the pattern observed in raw leachate. Removal efficiency of heavy metals was at the level of about 97–99%, which was comparable to observed by other authors. Ashes from Jaworzono PP were slightly more efficient in heavy metals removal from leachates than the ones from Turów

PP. Activation of fly ashes increased adsorption potential of fly ashes, both from Jaworzono and Turów PP. Removal efficiency of activated ashes was similar.

To evaluate the potential of fly ashes to immobilize the compounds which concentrations decreased, the most of analysed loads of pollutants were calculated. They are listed in Table 9. As can be seen from the analysis, control ashes from Jaworzono PP allowed for removal 36.5% of N-NH<sub>4</sub><sup>+</sup> present in landfill leachate inflow. Simultaneously 49.1% of TOC was removed. The use of columns packed with activated fly ashes increased the loads of ammonium nitrogen and TOC which were removed from the leachates. They were equal to 53.6 and 63.7%, for N-NH<sub>4</sub><sup>+</sup> and TOC, respectively. It means that mechanical activation of the sludge increased N-NH<sub>4</sub><sup>+</sup> load removal by 17.7% as well as TOC removal by 14% compared to control samples. Activation of fly ashes improved also at about one two per cent removal efficiency of most of heavy metals (Table 9).

Taking into consideration the loads of ammonium nitrogen and TOC which are annually discharged with leachates (e.g. flow of leachate equal to 40 m<sup>3</sup> d<sup>-1</sup>;

Table 9  
Loads of selected pollutants immobilized by activated and control ashes (not activated)

Fly ashes	Parameter	Load			Removal, %
		Introduced, mg	Not immobilized, mg	Immobilized, mg	
J control sample	N-NH <sub>4</sub> <sup>+</sup>	289.2	183.7	105.4	36.5
	TOC	383.4	195.0	188.4	49.1
	Zn	16.0	0.2	15.8	98.8
	Cu	16.0	0.2	15.8	98.8
	Ni	16.0	0.1	15.9	99.4
	Cd	16.0	0.1	15.9	99.4
J activated	N-NH <sub>4</sub> <sup>+</sup>	288.1	137.8	150.3	52.2
	TOC	382.0	139.3	242.7	63.5
	Zn	16.0	0.1	15.9	99.4
	Cu	16.0	0.1	15.9	99.4
	Ni	16.0	0.1	15.9	99.4
	Cd	16.0	0	16.0	100
T control sample	N-NH <sub>4</sub> <sup>+</sup>	289.2	203.7	85.4	29.5
	TOC	383.4	211.9	171.5	44.7
	Zn	21.6	0.4	21.2	98.1
	Cu	21.6	0.3	21.3	98.6
	Ni	21.6	0.3	21.3	98.6
	Cd	21.6	0.1	21.5	99.5
T activated	N-NH <sub>4</sub> <sup>+</sup>	288.1	202.7	85.4	29.6
	TOC	382.0	246.4	135.5	35.5
	Zn	16.0	0.2	15.8	98.8
	Cu	16.0	0.1	15.9	99.4
	Ni	16.0	0.2	15.8	98.8
	Cd	16.0	0.1	15.9	99.4

concentration of TOC equal to  $355 \text{ mgC L}^{-1}$ ; concentration of  $\text{N-NH}_4^+$  equal to  $230 \text{ mg L}^{-1}$ , the amounts of these pollutants caught by activated fly ash from Jaworzno PP are higher than not activated ashes by  $594 \text{ kg N-NH}_4^+$  and  $725 \text{ kg TOC}$ . Better effects of pollutants removal by activated fly ashes mixtures were connected with the changes of their permeability. Activation of ash caused the change in the value of permeability coefficient of solidified fly ashes (from  $1.54 \times 10^{-5}$  to  $5.46 \times 10^{-6} \text{ m/s}$ ).

In contrary to the results obtained for Jaworzno PP, mechanical activation of ashes from Turów PP was not effective. Fly ashes from Turów PP (the control sample) hold 29.5% of ammonium nitrogen load. Simultaneously, they immobilized 44.7% of TOC load. Mechanical activation of Turów PP ashes did not increase  $\text{N-NH}_4^+$  immobilization capacity and decreased TOC immobilization (by about 9%). It indicates that in the event that we would like to use mechanical activation the effectiveness of this process must be checked experimentally for individual ashes.

Concerning the use of fly ashes in ammonium nitrogen removal it should, however, be emphasized that ammonium nitrogen can be also leached from fly ashes. During the present investigation, one could observe a phenomenon similar to the chlorides. However, it cannot be excluded that also ammonium nitrogen will be leached from the ashes. Experiments done by Bittner et al. [18] indicate that leachability of ammonium from fly ashes is dependent on the equilibrium between ammonium ion and molecular ammonia which is affected by pH of the reaction environment.

The results obtained during the experiment indicate that fly ashes are a very promising alternative for other sorbents used in environmental engineering. Mechanical activation can increase immobilization properties of fly ashes, but it is not a rule. Every time experiments which will prove the fitness of mechanical activation for increasing immobilization effectiveness should be carried out.

#### 4. Conclusions

The conclusions are that mechanical activation of fly ashes from coal burning may positively affect

- (1) the value of the permeability coefficient (contact time of ashes and leachate elongates),
- (2) an increase in over 14% removal of TOC compared to not activated ashes,
- (3) 17.7% improvement of ammonium nitrogen immobilization compared to the control sample,
- (4) effectiveness of heavy metals removal (it must be emphasized that immobilization properties of fly ashes to heavy metals are very high also without the activation process).

The effect of mechanical activation on immobilization properties is closely connected with the kind of burned fossil fuels. Activation on ashes from lignite burning showed no increase in their immobilization properties.

#### Acknowledgements

This work was supported by the Częstochowa University of Technology project: BS-PB-402-301/2011.

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