

Fly Ash and Slug Mixture from Heat and Power Generating Plant as Environmentally Friendly Industrial Waste

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Abstract

Mixtures of fly ash and slugs were subjected to laboratory tests in order to estimate their influence on natural water and soil condition in order to check their possible application towards for recultivation or landfilling. The chemical composition of the mixtures and their extracts obtained with solutions of sulphuric acid (pH 2 or 4) as eluent (simulating acid rain) were determined. Assuming the criteria to be met by drinking water specified by the European Union and WHO documents, it was established that the heavy metals content in the fly ash and slug mixtures is not expected to have a negative effect on underground water.

Keywords! fly ash, slug, heat and power generating plant, environmental impact.

Introduction

In Poland mixtures of fly ash and slug, being waste products of heat and power generating plants, are stored in large masses. According to statistical data, they are the third waste product obtained annually by mass; in 1998 the mass of this industrial waste was 20.3 mln tons. The mixtures have been considered valuable waste, used for industrial purposes (road construction) and landscaping.

Economical use of fly ash and slugs from heat and power generating plants in Poznan for landfilling or recultivation of municipal dumping grounds has been much criticised for fear of the negative effects of the heavy metals they contain on the environment. Some sources have claimed that the heavy metals can be washed by acid rains and penetrate deeper layers of soil, contaminating underground waters. Poznan was the location of a long-lived controversy called "the ash war", which ended with the introduction of a government act classifying wastes in

which fly ashes were classified as environmentally harmless. However, even now the conviction of their harmful effect is widespread.

The interaction of fly ash on the environment can be realized through:

- Dusting of ash in periods of dry and windy weather, from heaps or during transportation in uncovered vehicles.
- Washing out soluble substances from the ash which can penetrate into surface and underground waters.

The dusting of ash can be limited or eliminated by wetting with water or covering with special emulsions, and transportation in covered vehicles. The washing out of ash components depends on the content and forms of the potentially harmful substances, type of eluents and conditions of their interaction.

In this context a study was undertaken to check the possibility of washing out water-soluble components from fly ash and slug mixtures, in particular heavy metals, in the conditions simulating acid rains. The study, whose results are reported in this work, was performed on

a waste material from the heat and power generating plant Karolin in Poznań, used in the form which is transported to dumping sites.

Materials and Methods

The material studied was two samples of a mixture of fly ash and slug (further referred to as ash) taken from the hydraulic ash-disposal grounds at the Karolin plant in Poznan. This disposal site is surrounded with earthen banks into which a pipeline supplies a mixture of water with slag and ash. The studied samples labelled as I and II were collected from the sites and layers representing ash stored for 5 and 15 years, respectively.

The samples were dried at $40 \pm 1^\circ\text{C}$ to constant mass and then ground in a ball mill. Portions of 5-10 g of prepared material were placed in conical flasks and subjected to 5-10 ml of concentrated hydrochloric acid. The acid was added dropwise under constant stirring. Having placed a funnel in the flask neck, the flask was left for 20 h (through the night). Then, the mixture in the flask was heated to boiling for 30 minutes. After the addition of 50 ml of ultrapure water (obtained in Milli-Q instrument) the mixture was heated again for 30 minutes. The hot content of the flask was filtered off through medium-pore-size paper filters (previously washed with ultrapure water) to the measuring flasks, and after cooling filled with ultrapure water to a volume of 100 ml.

In the solutions obtained the contents of the following elements were determined:

- Calcium and magnesium - by EDTA titration,
- Phosphates - by the spectrophotometric method with ammonium molybdate and ascorbic acid as a reducing agent,
- Sulphates - as barium sulphates by the gravimetric method,
- Chromium, zinc, cadmium, manganese, copper, nickel, lead, iron - by atomic absorption spectrometry AAS, with electrothermal atomisation, (on Spektr AA 20 Plus, Varian),
- Arsenic and antimony - by atomic absorption spectrometry with generation of hydrides (on Spektr AA 20 Plus, Varian),
- Sodium and potassium - by the emission atomic spectrometry (on Analyst 300, Perkin Elmer).

Apart from this the concentration of mineral components insoluble in hydrochloric acid and moisture content of the samples were determined. The content of mineral substances was determined in a residue obtained after ignition at 550°C of the insoluble parts kept by a paper filter after filtering the weighted portions of ashes subjected to the acid at a high temperature. In the spectrometric analyses of metal content a certified reference material for water SLRS-3 was used.

The degree of washing out of the water-soluble substances from the ash was studied using the procedure recommended by the Polish Standards [1]. To simulate the effect of acid rains of extreme pH, instead of distilled water, water solutions of sulphuric acid of pH 2 and 4 were applied. A weighted portion of $100 \text{ g} \pm 0.5 \text{ g}$ of dried and ground sample of the ash was placed in a bottle of 1000 ml, to which 900 ml of an appropriate solution of

sulphuric acid was added. The sealed bottle was placed in a rotating shaker for 4 h. After this time, the bottle was allowed to stand for 16 h and then the shaking was continued for another 4 hours. After leaving the bottle to stand until sediment was formed, the solution from above the sediment was poured out and the residual mixture was centrifuged. The obtained extract (combined decanted liquid and supernatant) was subjected to analysis. The ash remaining in the bottle was again flooded with a solution of sulphuric acid of pH 2. The bottle was mounted in a shaker and the process of washing out was ten times repeated, using a solution of sulphuric acid of pH 2 as eluent.

The extracts from the ash samples with the use of sulphuric acid of pH 4 were obtained in the same way. For each sample 5 parallel extractions were made using the acid of each pH value. In the water extracts we determined pH, calcium, magnesium, chromium, cadmium, manganese, copper, nickel, lead, potassium, sodium and iron by the same methods as those used in analysis of fly ash and slug mixture samples.

Results and Discussion

Table 1 shows the results of analysis of the two samples of ash. The values are averages of 5 parallel determinations. Except for moisture content, the concentrations of all components are expressed in dry mass.

Table 1. Chemical composition of the ash samples.

Component	Sample I	Sample II
Moisture content, %	0.86	1.05
Mineral components insoluble in HCl, g/kg	842	938
Calcium, g/kg	17.0	18.14
Magnesium, g/kg	9.71	7.38
Iron, g/kg	15.2	12.5
Potassium, g/kg	2.20	2.19
Sodium, g/kg	0.59	0.69
Manganese, g/kg	0.23	0.53
Sulphides, g/kg SO_4^{2-}	18.1	20.0
Phosphates, g/kg PO_4^{3-}	3.50	3.23
Cadmium, mg/kg	1.32	0.85
Chromium, mg/kg	31.4	20.3
Copper, mg/kg	56.6	24.9
Nickel, mg/kg	31.8	34.7
Lead, mg/kg	30.2	21.6
Zinc, mg/kg	88.3	53.3
Arsenic, mg/kg	0.11	0.06
Antimony, mg/kg	0.012	0.012

Table 2. The contents of Ca, Mg, Na, K, Fe and Mn in ash extracts obtained with a sulphuric acid solution of pH 2.

Extract no.	pH*	Contents of metals in mg/l (I – in sample I extracts, II – in sample II extracts)											
		Calcium		Magnesium		Sodium		Potassium		Iron		Manganese	
		I	II	I	II	I	II	I	II	I	II	I	II
1	9.77	60.5	36.0	28.6	6.9	7.9	8.1	9.9	11.3	0.31	0.06	0.004	0.003
2	9.08	80.8	70.5	19.4	16.3	1.6	2.8	4.2	5.6	0.03	0.02	0.004	0.005
3	8.45	51.4	50.0	16.8	7.1	0.4	0.8	1.5	2.6	0.01	0.02	0.003	0.005
4	8.39	46.6	48.9	21.2	15.8	0.2	0.4	1.0	1.7	0.01	0.01	0.003	0.007
5	8.33	41.7	42.6	14.4	9.0	0.5	0.7	0.7	1.1	0.02	0.02	0.004	0.006
6	8.03	38.0	40.6	17.0	9.4	0.3	0.4	0.5	0.9	0.03	0.13	0.002	0.008
7	7.53	42.6	46.1	10.9	6.2	0.2	0.3	0.5	0.9	0.01	0.02	0.003	0.008
8	7.37	31.8	34.1	10.0	6.8	0.2	0.3	0.4	0.7	0.06	0.03	0.005	0.008
9	7.01	24.3	25.1	6.1	3.3	0.1	0.2	0.4	0.5	0.03	0.03	0.003	0.007
10	6.88	28.4	24.4	8.0	5.2	0.2	0.3	0.4	0.7	0.03	0.01	0.005	0.004

* mean value for extracts from the two samples

The chemical composition of ash depends on many factors: the quality of fuel, conditions of combustion, method of removal, and time and conditions of storage prior to further use. As mentioned above, the samples were collected from ash deposits stored in open air for 5 and 15 years. For all these years the ash has been influenced by atmospheric factors, e.g. washed out by rain. This fact is reflected in the content of mineral components soluble in hydrochloric acid, which is lower than in other ash [2]. First of all, our samples contained smaller amounts of heavy metals, whose concentrations were of the same order as in naturally pure soils in Poland [3, 4].

Results of determinations of the ability of washing out the ash components by sulphuric acid solutions of pH 2 or 4, are shown in Tables 2-5. As specified in the description of the procedure, the weighted portions of the ash were treated by 10 successively applied volumes of

the acid solutions, keeping the mass ratio of the eluent to the ash as 1:9. pH value was determined after each extraction.

As follows from the above presented results, the ability of washing out heavy metals from the ash by diluted solutions of sulphuric acid - simulating the effect of acid rain - is very small. The main reason for this seems to be the form of the chemical components in the ash, which contain large amounts of amorphous vitreous substances with occluded heavy metals and trace amounts of crystalline substances. The latter contain mullite $3Al_2O_3 \cdot 2SiO_2$, dicalcium ferrite $2CaO \cdot Fe_2O_3$, anatase TiO_2 , corundum Al_2O_3 and calcium oxide CaO . The iron compounds are most often found as magnetite $FeO \cdot Fe_3O_4$. The ash moreover contains quartz and particles of not-combusted but degassed coal. The ash grains formed of not fully calcined clay substances are characterized by a porous structure of dehydrated metacaolinite $2SiO_2 \cdot Al_2O_3$.

Table 3. The contents of heavy metals in ash extracts obtained with a solution of sulphuric acid of pH 2.

Extract no.	Contents of heavy metals in mg/l (I – in sample I extracts, II – in sample II extracts)											
	Cadmium		Chromium		Copper		Nickel		Lead		Zinc	
	I	II	I	II	I	II	I	II	I	II	I	II
1	0.003	0.001	0.008	0.008	0.005	0.003	0.004	0.001	0.006	0.002	0.010	0.009
2	0.004	0.001	0.009	0.009	0.004	0.003	0.001	0.001	0.007	0.004	0.009	0.011
3	0.004	0.002	0.009	0.006	0.003	0.003	0.000	0.000	0.008	0.004	0.005	0.009
4	0.005	0.002	0.007	0.005	0.003	0.002	0.000	0.000	0.008	0.005	0.004	0.004
5	0.007	0.004	0.008	0.003	0.004	0.003	0.000	0.000	0.008	0.005	0.006	0.008
6	0.009	0.005	0.007	0.004	0.002	0.003	0.001	0.001	0.007	0.006	0.005	0.008
7	0.011	0.005	0.005	0.003	0.004	0.003	0.002	0.001	0.007	0.006	0.018	0.014
8	0.011	0.006	0.004	0.001	0.003	0.002	0.001	0.001	0.007	0.006	0.005	0.007
9	0.009	0.005	0.004	0.000	0.004	0.003	0.002	0.001	0.006	0.007	0.024	0.051
10	0.005	0.005	0.002	0.000	0.004	0.003	0.000	0.007	0.006	0.007	0.017	0.011

Table 4. The contents of Ca, Mg, Na, K, Fe and Mn in ash extracts obtained with a sulphuric acid solution of pH 4.

Extract no.	pH*	Contents of metals in mg/l (I – sample I extracts, II – sample II extracts)											
		Calcium		Magnesium		Sodium		Potassium		Iron		Manganese	
		I	II	I	II	I	II	I	II	I	II	I	II
1	9.80	37.1	31.6	16.2	9.1	10.4	11.5	12.7	12.5	0.006	0.011	0.001	0.002
2	9.12	20.9	14.2	13.0	7.8	1.6	2.3	3.8	4.7	0.014	0.008	0.001	0.001
3	8.55	18.8	18.0	12.5	7.2	1.4	3.2	3.6	4.6	0.010	0.008	0.001	0.000
4	8.39	14.6	15.5	11.3	7.0	1.1	3.1	3.4	4.0	0.009	0.007	0.001	0.001
5	8.26	12.6	10.7	9.1	6.1	0.9	0.8	2.2	2.1	0.008	0.006	0.002	0.002
6	8.13	10.6	8.6	8.0	5.0	0.6	0.4	1.7	1.3	0.010	0.009	0.002	0.002
7	7.88	9.9	8.5	5.4	4.8	0.4	0.4	0.8	0.7	0.01	0.03	0.004	0.002
8	7.47	9.2	8.4	4.9	4.6	0.2	0.3	0.4	0.7	0.02	0.01	0.005	0.004
9	7.28	9.0	8.0	4.4	4.5	0.3	0.3	0.4	0.5	0.02	0.02	0.003	0.007
10	7.05	8.8	8.0	3.8	4.0	0.2	0.3	0.4	0.6	0.01	0.01	0.004	0.004

* mean value for extracts from the two samples

Table 4. The contents of Ca, Mg, Na, K, Fe and Mn in ash extracts obtained with a sulphuric acid solution of pH 4.

Extract no.	pH*	Contents of metals in mg/l (I – sample I extracts, II – sample II extracts)											
		Calcium		Magnesium		Sodium		Potassium		Iron		Manganese	
		I	II	I	II	I	II	I	II	I	II	I	II
1	9.80	37.1	31.6	16.2	9.1	10.4	11.5	12.7	12.5	0.006	0.011	0.001	0.002
2	9.12	20.9	14.2	13.0	7.8	1.6	2.3	3.8	4.7	0.014	0.008	0.001	0.001
3	8.55	18.8	18.0	12.5	7.2	1.4	3.2	3.6	4.6	0.010	0.008	0.001	0.000
4	8.39	14.6	15.5	11.3	7.0	1.1	3.1	3.4	4.0	0.009	0.007	0.001	0.001
5	8.26	12.6	10.7	9.1	6.1	0.9	0.8	2.2	2.1	0.008	0.006	0.002	0.002
6	8.13	10.6	8.6	8.0	5.0	0.6	0.4	1.7	1.3	0.010	0.009	0.002	0.002
7	7.88	9.9	8.5	5.4	4.8	0.4	0.4	0.8	0.7	0.01	0.03	0.004	0.002
8	7.47	9.2	8.4	4.9	4.6	0.2	0.3	0.4	0.7	0.02	0.01	0.005	0.004
9	7.28	9.0	8.0	4.4	4.5	0.3	0.3	0.4	0.5	0.02	0.02	0.003	0.007
10	7.05	8.8	8.0	3.8	4.0	0.2	0.3	0.4	0.6	0.01	0.01	0.004	0.004

* mean value for extracts from the two samples

[5, 6]. The metal oxides found in the ash reveal a low solubility in diluted solutions of mineral acids.

An additional barrier preventing the washing out of metals is the alkaline pH of the ash, which in our experiments was neutralized only after the addition of 9000 ml of the diluted sulphuric acid to 100 g portions of the ash.

According to our analyses, the concentration of heavy metals (potentially most harmful components) in the extracts studied was mostly at the level of 10^{-3} mg/l, and only in some cases reached 10^{-2} mg/l. Concentrations at these levels cannot have a harmful effect on the environment (underground waters) because metal content in the extracts did not exceed concentrations recommended by WHO in drinking water [7]. According to Polish and EU requirements [8, 9], the maximum allowable concentrations of the most important metals are: 0.003 and 0.005 mg/l Cd; 0.01 and 0.01 mg/l Pb; 0.05 and 0.05 mg/l Cr;

0.01 and 0.01 mg/l As. The results also show that the ash and slug wastes deposited for a long time before their economical use meet the criteria of the European Union act classification as materials of no harm to the environment [10]. They also justify a similar classification adopted by Polish law [11].

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