Examination of fly-ashes stored in workings of „Wujek" coal mine in aspect of their influence on environment

Edward Cempiel[1], Krystyna Grabowska[1], Marek Pozzi[1], Małgorzata Sowa[1]

[1]*Silesian University of Technology, Department of Applied Geology, Akademicka 2, 44-100 Gliwice, e-mail: cempiel@geo.gorn.polsl.gliwice.pl*

Abstract: Samples of fly-ashes remaining in mining workings of "Wujek" coal mine since 1995-96 were analysed. These fly-ashes include over 10 times greater quantity of soluble components than fresh fly-ashes (mainly chlorides and sulfides) of which over 70% were leached already after 24 hours. In case of contact of fly-ashes with fresh water due to the changes of hydrogeological regime resulting from coal mine closing, deterioration of quality of these waters shall follow.

1 INTRODUCTION

Waste materials from power plant, including fly-ashes, make approximately 18.5% of industrial waste produced, whereas their quantity is approximately 26 million Mg per year.

Problem of fly-ashes management is specially significant for Silesian area because of limited area for direct storing and also of special arduousness for environment when waste are deposited on Earth surface.

One of economical methods of waste materials management is depositing them in underground workings of coal mines to make abandoned workings more packed, to liquidate workings as well as anti-fire prophylactics purposes. Quantity of deposited ashes still increases and at present it makes about 50% of general quantity of ashes produced by power plants of Południowy Okręg Energetyczny (South Power Industry Region). This method of fly-ashes utilisation has also other positive ecological aspects. This is an effective way to reduce subsidence and deformation of surface and also mining salty waters management used to prepare ash-water mixture (an emulsifying agent), in which ash to water mass ratio is 1:3 to 1:1 (Żmij et al.,1994 and Pozzi & Pozzi, 1996). Negative aspect of this ashes utilisation method is its influence on reaction change and chemical composition of mine water just after being deposited as well as during later period of time, during liquidation of mines because waste waters show increased value of pH up to 12, whereas the permissible value is 9, as well as increased content of sulfates, which exceeds admissible concentration in waste water discharged to waters and to the ground, i.e. 500 mg/dm^3.

2 PURPOSE AND SCOPE OF EXAMINATIONS

Authors' examinations related to influence of ashes components on mine water environment include ashes from El. Łaziska (Łaziska Power Plant) and El. Łagisza (Łagisza Power Plant), being deposited in workings of "Wujek" Coal Mine belonging to Katowicki Holding Węglowy (Katowice Mining Holding). "Wujek" Coal Mine is one of 8 mines of the holding, in which fly-ashes are deposited in an amount about 650 thousand Mg/month, including 145 Mg/y in "Wujek" Coal Mine.

Examinations included ashes which remained in mining workings several years – ashes from El. Łaziska since 1995 (Arkona cross-cut, level 613 m.) and ashes from El. Łagisza since 1996 (West rise gallery 7a located in coal bed 510) (Grabowska et al., 1999).

To determine their influence on water environment, examinations were by means of carried out as follows:

- physical properties and chemical composition,
- leaching using static method,
- leaching infiltrating distilled and mine water (dynamic method).

Examinations allowed to draw conclusions related to fly-ashes influence on mine waters after several years of storing; this fact is significant for prognosis of contamination migration in rock mass caused with alterations of hydrogeological conditions in case of liquidation of a mine.

3 PHYSICAL PROPERTIES AND CHEMICAL COMPOSITION OF ASHES

Fly-ashes, being deposited in workings of „Wujek" Coal Mine make fine dispersion (about 80% of fraction is composed of grains below 0.1 mm), of very large porosity (n = 44 – 52%). As a result of long-term storage, some their physical properties change (Table 1). As a result of compaction their porosity decreases (n = 10.93 – 12.87%), they are slightly permeable, at filtration coefficient of 10^{-6} m/s.

Table 1 Physical properties of fly-ashes from „Wujek" coal mine

Sample	Density ρ_s (g* cm^{-3})	Bulk density ρ_o (g* cm^{-3})	Porosity index n (%) Conditions		Storage coefficient (μ)	Hydraulic conductivity k (m/s)
			Non compacted	Compacted		
1 - Łaziska Pp	1.92	1.73	44.0	10.93	0.08 – 0.11	1.256 E^{-06} -2.845 E^{-06}
2 - Łagisza Pp	2.02	1.78	52.0	12.87	0.09 – 0.12	2.204 E^{-06} -3.459 E^{-06}

Bleeding coefficient (μ) from 0.08 up to 0.12 shows slight quantity of water bleeding from emulsifying agent.

Ashes under examination are characterised with similar chemical composition (Table 2). They are typical silicate ashes which are created during coal combustion without desulfurization of waste gas of content SiO_2 and Al_2O_3 about 70% and CaO within the range of 3 –5.5%. They have slight solidification properties. Of trace elements, Zn occurs most frequently (272 ppm) and Pb (217 ppm).

Table 2 Chemical composition of fly-ashes

Chemical components	Unit	Łaziska Power Plant	Łagisza Power Plant
SiO_2	%	42.67	45.01
Al_2O_3	%	29.57	25.67
Fe_2O_3	%	8.16	10.13
CaO	%	3.16	5.47
MgO	%	3.51	2.46
Na_2O	%	0.36	0.38
K_2O	%	0.19	0.20
Humidity	%	1.79	0.95
Weight loss	%	10.17	9.47
Zn	ppm	161	272
Cd.	ppm	<3	<4
Cu	ppm	158	114
Pb	ppm	198	217
Ni	ppm	120	150
Cr	ppm	132	112
Mn	ppm	210	204

4 PERMEABILITY OF ASHES IN WATER

4.1 Leaching of ashes with distilled water using static method

Leaching of fly-ashes, using static method was done by leaching test with distilled water, when the ratio of water to fly-ashes is 10:1. The chemical analysis of oversediment water were done during leaching: 1, 6, 15 and 30 days (Table 3, Figure.1).Ashes, after 4-5 years from date of storage in mining workings contain from 5.68% up to 5.04% of soluble parts, mainly chlorides. Course of leaching during 30 days shows that this process runs very quickly and already after 24 hours 80 percent of chlorides were leached; sulfates are leached a little more slowly. Water reaction of leaching the wastes is slightly alkaline, maximum up to 7.91 pH. Ashes collected from mining workings contain over 10-fold more soluble components than these coming directly from power plant (Pozzi & Pozzi, 1996). They are adsorbed from salty mine water used to transport ashes by means of hydraulic methods. Of fresh waste materials, sulfates are leached most frequently (Grabowska et al., 1999), instead of stored chlorides. Waste materials, after several years of storage, do not cause alkalisation of reaction of waters which are in contact with them.

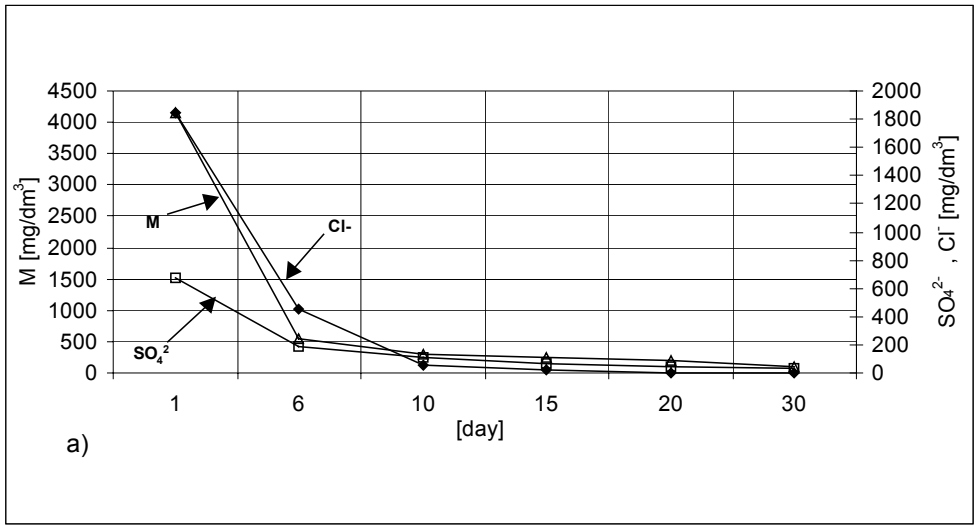
4.2 Leaching of ashes with distilled water using dynamic method

On the basis of tests made in rectifying column it was found that quantity of leached soluble parts was 6.76% up to 5.5% of ashes mass (Table 4). During filtration, a little more soluble components are leached from waste materials than in case of lentic water. Type of leached components and the method of their leaching are the same as in case of static method. The most quantity as well as most quickly (the first dm^3 of water leaches over 76% of all soluble components of a sample) chlorides are leached, then sulfates, whose leaching process runs slower (Figure. 2).

Table 3 Leaching of fly-ashes from „Wujek" coal mine with water using static method

Components	Unit	Łaziska Power Plant				Łagisza Power Plant			
		Time of leaching test [day]							
		1	6	15	30	1	6	15	30
pH	-	7.47	7.91	7.50	7.02	7.71	7.49	7.55	7.1
Mineralisation	Mg/dm^3	4190	518	296	108	3858	468	202	108
Alcalinity	$Mval/dm^3$	1.00	0.8	0.6	0.4	1.6	1.0	1.0	0.8
Carbonaty hardness	^0n	2.8	2.24	1.68	1.12	4.49	2.8	2.8	2.24
Total hardness	^0n	90.85	16.82	8.97	13.42	68.42	15.70	11.21	13.46
Calcium hardness	^0n	79.63	13.46	7.85	11.22	54.96	12.34	8.97	8.97
Cl^-	mg/dm^3	1853.1	227.2	14.2	t.	1696.9	184.6	14.2	t.
SO_4^{2-}	mg/dm^3	683.1	114.4	77.93	42.12	468.38	122.69	56.37	27.7
HCO_3^-	mg/dm^3	60.76	48.61	36.46	24.30	97.43	60.76	60.76	48.61
Ca	mg/dm^3	569.14	96.19	56.12	80.16	392.78	88.18	64.13	64.12
Mg	mg/dm^3	48.64	14.60	4.86	9.73	58.37	14.60	8.97	8.97
Zn	mg/dm^3	0.015	-	-	n.e.	0.023	-	-	n.e.
Cd	mg/dm^3	n.e.	-	-	n.e.	n.e.	-	-	n.e.
Pb	mg/dm^3	0.025	-	-	0.005	0.027	-	-	0.01
Cu	mg/dm^3	< 0.02	-	-	n.e.	0.025	-	-	n.e.
Ni	mg/dm^3	0.024	-	-	0.015	0.030	-	-	0.015
Cr	mg/dm^3	0.021	-	-	0.004	0.048	-	-	0.005
Solube compo-nents leached	%	4.19	0.52	0.30	0.11	3.86	0.47	0.20	0.11
Σ of soluble components leached during test	%	5.68				5.04			

Weight of sample m = 100 g, - not examinated, n.e.- no exist, t – traces



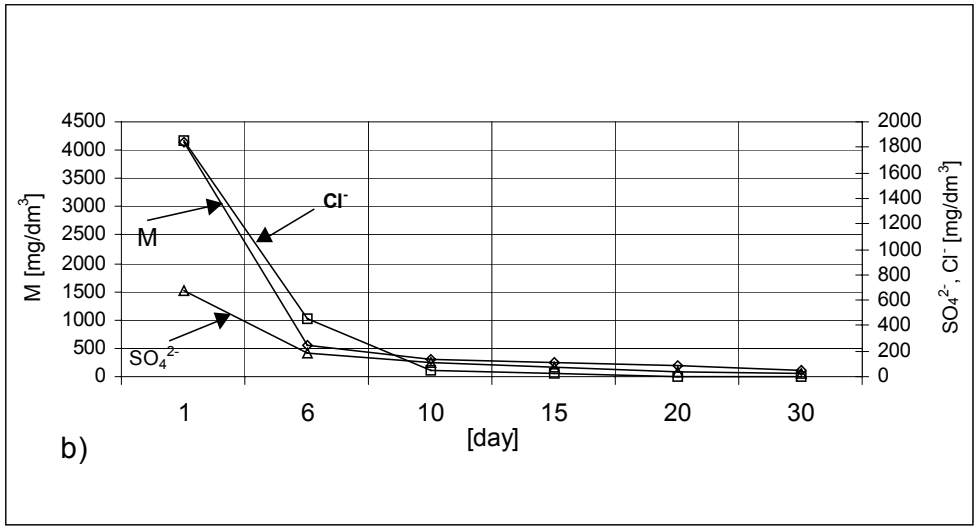


Figure 1 Changes of mineralization, chlorides and sulphates content during leaching test of fly-ashes using static method

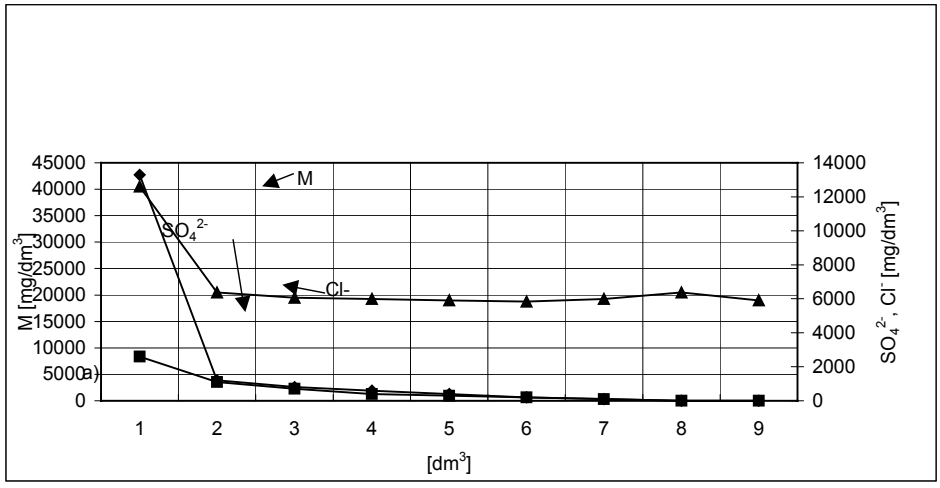
a) fly-ashes from Łaziska power plant

b) fly-ashes from Łagisza power plant

Table 4 Analysis of leachate of fly-ashes from „Wujek" coal mine with distilled water using dynamic method

Components	Unit	Łaziska Power Plant			Łagisza Power Plant		
		Following dm^3 of water					
		1	2	10	1	2	10
pH	-	7.56	7.37	7.49	7.73	7.45	7.30
Mineralisation	mg/dm^3	25816	2972	152	32572	3064	112
Alcalinity	$mval/dm_3$	2.4	1.8	0.4	2.8	1.6	0.4
Carbonaty hardness	^0n	6.73	5.05	1.12	7.85	4.49	1.12
Total hardness	^0n	318.53	139.08	13.46	318.53	141.32	6.73
Calcium hardness	^0n	251.24	130.1	8.97	214.23	134.59	4.49
Cl^-	mg/dm^3	13064	49.7	t.	10579	49.7	t.
SO_4^{2-}	mg/dm^3	2642.8	1148.2	39.8	18255	12485	33.9
HCO_3^-	mg/dm^3	146.04	109.6	24.30	170.3	97.4	24.30
Ca	mg/dm^3	1795.58	929.86	64.13	1531.1	961.92	32.06
Mg	mg/dm^3	291.84	38.91	19.46	452.35	29.18	9.73
Zn	mg/dm^3	0.062	-	n.e.	0.032	-	n.e.
Cd.	mg/dm^3	n.e.	-	n.e.	n.e.	-	n.e.
Pb	mg/dm^3	0.054	-	0.036	0.05	-	0.04
Cu	mg/dm^3	0.008	-	<0.002	0.031	-	0.02
Ni	mg/dm^3	0.05	-	0.025	0.05	-	0.03
Cr	mg/dm^3	0.032	-	0.007	0.066	-	0.008
Soluble compo-nents leached	%	5.16	0.59	0.03	4.21	0.61	0.02
Σ of soluble components leached during test	%	6.76			5.50		

Weight of sample m = 500g, - not examinated, n.e.- no exist, t - traces



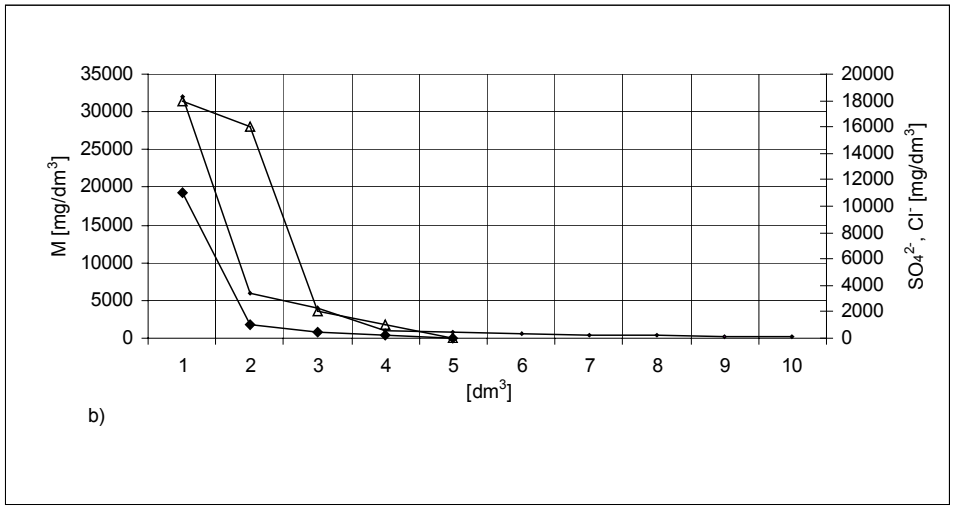


Figure 2 Changes of mineralization, chlorides and sulphates content during leaching test of fly-ashes using dynamic method with distilled water

a) fly-ashes from Łaziska power plant

b) fly-ashes from Łagisza power plant

4.3 Leaching of ashes with mine water using dynamic method

To find how leaching process is performed of soluble parts from waste materials through infiltrating underground waters, model examinations were carried out by filtering waste materials with mine water collected from mining workings of „Wujek" Coal Mine from the level, where ashes were stored. This is highly mineralised water, of mineralization 19697 mg/dm^3, slightly alkaline, very hard, of chlorides content of 9585 mg/dm^3 and sulfates 1046.2 mg/dm^3 (Table 5). Through samples of waste materials of 500 g mass each, 9 dm^3 of mine water was filtered in total. Each dm^3 of filtrate was chemically analysed, the results of which are presented in Table 6 and in Figure. 3.

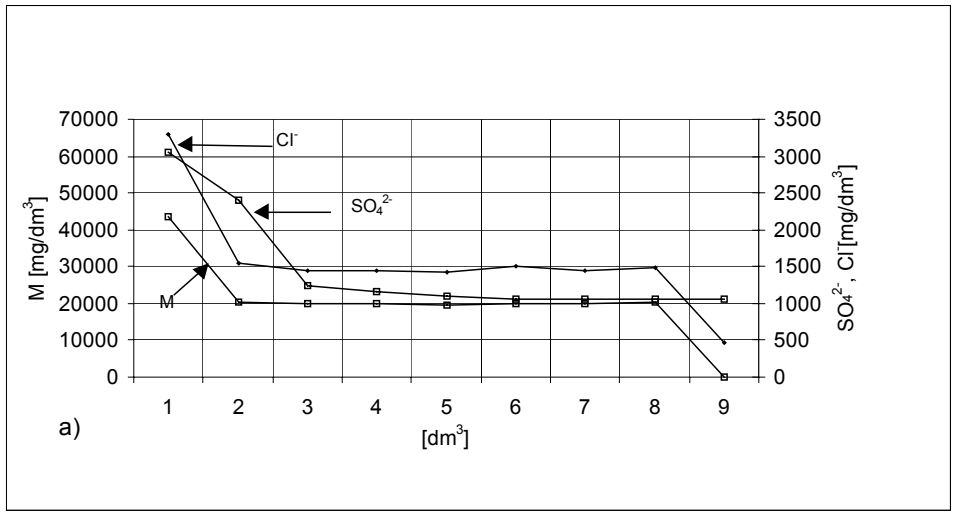
Table 5 Chemical analysis of drainage water from „Wujek" coal mine

Components	Unit	Quantity
pH	-	7.31
Mineralisation	mg/dm^3	19697.0
Alcalinity	mval/dm^3	4.25
Carbonaty hardness	^{0}n	11.91
Total hardness	^{0}n	340.2
Calcium hardness	^{0}n	161.4
Cl^-	mg/dm^3	9585.0
SO_4^{2-}	mg/dm^3	1046.2
HCO_3^-	mg/dm^3	258.5
Ca	mg/dm^3	1154.3
Mg	mg/dm^3	775.8
Fe	ppm.	0.215
Zn	ppm.	0.24
Cd.	ppm.	0.006
Pb	ppm.	0.323
Cu	ppm.	0.015
Ni	ppm.	0.224
Cr	ppm.	0.015

Table 6 Leaching of fly-ashes with mine water using dynamic method

Components	Unit	Łaziska Power Plant			Łagisza Power Plant		
		Following dm^3 of water					
		1	2	9	1	2	9
pH	-	6.76	7.21	7.47	7.81	7.91	7.70
Mineralisation	mg/dm^3	43310	20754	19544	40144	20964	19156
Alcalinity	$mval/dm^3$	4.2	4.0	4.4	2.6	2.2	4.2
Carbonaty hardness	^0n	11.78	11.2	12.3	7.29	6.17	11.78
Total hardness	^0n	627.4	481.7	358.5	616.2	504.2	358.5
Calcium hardness	^0n	436.9	313.7	168.1	470.6	347.3	168.1
Cl^-	mg/dm^3	22542	10472	9727	20412.5	9940	9798
SO_4^{2-}	mg/dm^3	3019.2	2320.3	1085.1	3089.6	2507.7	1085.3
HCO_3^-	mg/dm^3	255.6	243.4	267.8	158.19	133.9	255.6
Ca	mg/dm^3	3126.2	2244.5	1202.4	3366.7	2484.9	1202.4
Mg	mg/dm^3	826.9	729.6	875.5	632.3	680.9	826.9
Zn	mg/dm^3	0.092	-	n.e.	0.031	-	n.e.
Cd.	mg/dm^3	<0.003	-	n.e.	<0.003	-	n.e.
Pb	mg/dm^3	0.146	-	0.036	0.16	-	0.05
Cu	mg/dm^3	0.036	-	<0.002	0.04	-	0.02
Ni	mg/dm^3	0.057	-	0.025	0.063	-	0.03
Cr	mg/dm^3	0.05	-	0.008	0.06	-	0.006
+increase/ - decrease of mine water mineralisation	mg/dm^3	+23613	+1057	-153	+ 20447	+1267	- 541
Leached soluble components	%	4.72	0.21	-0.031	4.09	0.25	-0.108
Σ of leached components during 30 days test	%	5.36			4.50		

Weight of sample m = 500 mg. - not examinated. n.e.- no exist



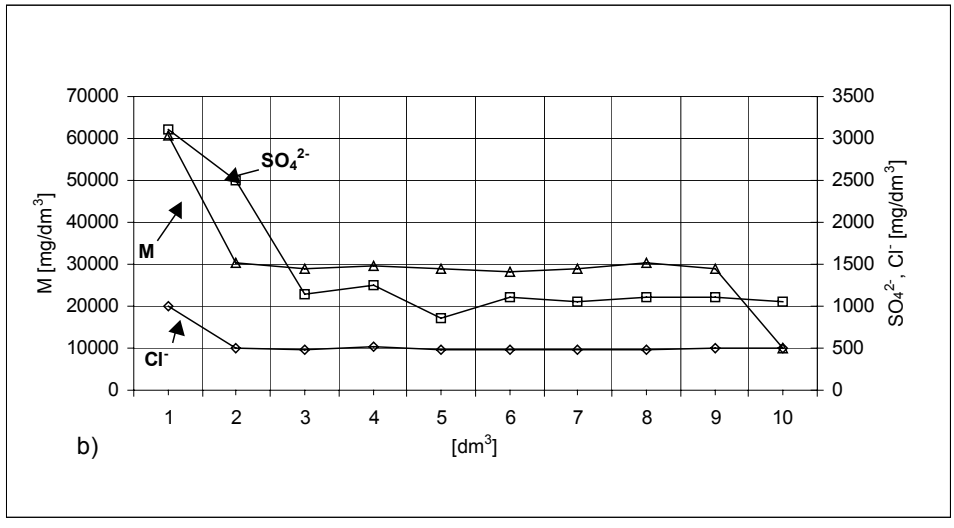


Figure 3 Changes of mineralization. chlorides and sulphates content during leaching test of fly-ashes using dynamic method with mine water

a) fly-ashes from Łaziska power plant

b) fly-ashes from Łagisza power plant

In total. mine water leached from ashes 26827 up to 22507 mg of soluble parts that makes 5.36 up to 4.5 % of waste materials. Mining water leaches soluble parts less than distilled water (about 1%). In case of 3. 4 as well as 9 dm^3. mineralization of filtrate is even lesser than mine water itself. because part of its

components is absorbed. Leaching process is alike as during filtration of distilled water. Significant increase of mineralization of the first dm^3 of filtrate occurs. caused mainly by total leaching out of chlorides contained in ashes. Sulfates are leached more slowly but their quantity increases significantly (1 and 2 dm^3 of filtrate). in relation to their content in mine water. Summing up. one may state that mine water. while filtering through waste materials (1 dm^3 of filtrate) at the beginning increases twice its mineralization. chlorides content increases also twice. and sulfates three times. whereas second dm^3 of filtrate is characterised with slight increase of mineralization and chlorides concentration. whereas sulfates content is twice higher than in mine water. Further dm^3 of filtrate (from 3 up to 9) do not change significantly the chemical composition of water.

Waste materials only slightly alkalise mine water. whose pH 7.31 (after filtration) increases up to 7.42 – 8.22.

5 CONCLUSIONS

Fly-ashes under analysis from "Łaziska" Power Plant and "Łagisza" Power Plant. stored in workings of „Wujek" Coal Mine belong to silicate ashes of low content of CaO (below 10%) and they have not self-solidification properties. Their chemical composition shows considerable content of iron (above 8% in terms of Fe_2O_3). which is not. however. dissolved by water. because it exists mainly in form of sulfides. Of trace elements. whose content is very small. zinc occurs in greater quantities (up to 272 ppm) and lead (217 ppm).

As bulk mass. ashes are strongly porous (n = 44% - 52%). After long-term storing (4 –5 years) they subject to compaction. their porosity decreases up to 10.93 % and 12.87 %. they are slightly soluble and show low filtering off (μ = 0.08 – 0.12).

Ashes stored several years in mining workings include considerably higher (over 10 times) quantity of soluble components than fresh fly-ashes. because chlorides and sulfides from underground waters. applied to prepare ashes - water mixture. had been adsorbed by them. By means of static method. 5.68 % up to 5.04 % were leached. whereas after 24 hours over 70% of soluble parts were leached. because easily soluble chlorides are their main part. As a result of leaching with distilled water by means of dynamic method 6.76% up to 5.5% of soluble parts were leached from waste materials. Filtering water has . however. slightly higher ability of leaching than lentic water. Strongly mineralised mine water has weaker leaching abilities of soluble parts from ashes than distilled water. As a result of filtration of mine water of mineralization about 20 g/dm^3 through waste materials. 5.36% up to 4.5 % of soluble parts were leached.

If fresh ashes cause considerable alkalisation of water (above 10 pH) thus after several years of storing in mining workings. reaction of water being in contact with waste materials does not exceed 7.91 pH and is slightly alkaline or neutral.

Trace elements (Zn. Pb. Ni. Cr. Mn) are being leached of very small quantities. from 0.002 up to 0.062 ppm and they shall have no effect on contamination of mine water.

Fly-ashes. stored in mining workings. subjected to activity of mine water as an alteration of hydro-geological regime. at the beginning of leaching period shall cause mainly increase of content of sulfates in mine water. and they shall cause alkaline reaction of these waters. Slight increase of mineralization of water by leaching of chlorides and sulfates from ashes in case of salty mine water has no significant meaning. In case of contact of ashes with fresh water. deterioration of quality of these waters shall follow.

REFERENCES

Cempiel E.. Grabowska K.. Sowa M.. 1993. Mineralization of Mine Water through Post-floatation Waste Materials and Smoke-box Dusts Stored in Mine Workings of Zabrze-Bielszowice Coal Mine. *Materials of International Conference. 1st Geo-mechanical School.* Ustroń (in Polish).

Grabowska K.. Sowa M.. Nowińska K.. 1999. *Determination of Physical and Chemical and Hydro-geological Properties of Samples of Power Industry Waste Materials Collected from Old Mine Workings of "Wujek" Coal Mine.* Report of BK-246 Work-Environment Geology and Hydro-geology Plant of Silesian Technical University. Gliwice (in Polish).

Grabowska K.. Sowa M.. 1996. Examinations of Fly-ashes form Rybnik Power Plant in Ecological Aspect. *Scientific Notebooks of Silesian Technical University. s. Mining. notebook No. 230.* Gliwice (in Polish).

Pozzi B.. Pozzi M.. 1996. Ecological Aspects of Storing Industrial Waste Materials in Underground Workings of Mines of Katowice Mining Holding. *Scientific Papers of GIG. Conference No. 13.* Katowice (in Polish).

Żmij M.. Bromek T.. Adamska-Kawalec E.. Mastalerz J.. 1994. Hydro-geological and hydro-chemical aspects of storing industrial waste materials. *Papers of 5th Conference "Problems of Geology and Ecology in underground mining".* Szczyrk (in Polish).

Badania popiołów lotnych zdeponowanych w wyrobiskach KWK „Wujek" w aspekcie ich wpływu na środowisko

Edward Cempiel, Krystyna Grabowska, Marek Pozzi, Małgorzata Sowa

Streszczenie: Przedstawiono wyniki badań podstawowych własności popiołów lotnych pobranych z wyrobisk górniczych kopalni „Wujek" z rejonów ich długoletniego składowania. Badania obejmują analizę składu chemicznego odpadów , ich własności fizycznych i hydrogeologicznych oraz ługowania części rozpuszczalnych w warunkach statycznych i dynamicznych. Uzyskane wyniki pozwolą na ocenę procesu migracji zanieczyszczeń w górotworze na skutek zmian warunków hydrogeologicznych w wyniku likwidacji kopalń.