ACID MINE DRAINAGE TREATMENT BY ASH FROM WOODEN CHIP COMBUSTION: STUDY OF MINE WATER COMPOSITION IN DEPENDENCE ON THE ASH DOSE AND DURATION OF MUTUAL INTERACTION

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Abstract: The biomass ash (BA) from wooden chip combustion was used in the treatment of acid mine drainage (AMD) from open cast brown coal mining in the Czech Republic. The used AMD is characteristic of high contents of SO_4^{2-} (1576 mg.l^{-1}), Fe (20 mg.l^{-1}), Al (15 mg.l^{-1}), Mn (5 mg.l^{-1}) and low pH (2.7), which need to be adjusted. The biomass ash samples were obtained through the combustion of wooden chips in an industrial boiler in Hodonín Power Plant, Czech Republic, and they predominantly contain SiO_2 (45 wt.%), CaO (17 wt.%), Al_2O_3 (13 wt. %), MgO (6 wt.%), Fe_2O_3 (4 wt.%), K_2O (3 wt.%), SO_3 (3 wt.%), P_2O_5 (2 wt.%), unburnt materials and metals. The AMD treatment process included dosing of biomass ash (doses of 2.9 g, 6 g and 20 g of BA) to adjust the pH values to 8, 10, 12. The experiments observed the pH values and turbidity in selected time intervals within 7 days. Samples were analysed for metal contents, which had been abundant either in AMD or ash, or in AMD and ash simultaneously, in selected times of occurrence of the changes in pH and turbidity. After treatment by biomass ash (at the end of the experiment after dosing of 2.9 g, 6 g and 20 g of BA), the AMD was examined for the concentrations of Ca (449, 422 and 376 mg.l^{-1}), Mg (135, 82 and 7 mg.l^{-1}), K (14, 21 and 54 mg.l^{-1}), Na (127, 123 and 172 mg.l^{-1}), Fe (below the detection limit (bd) in all cases), Mn (1.4, 0.063 mg.l^{-1} and bd), Al (bd in all cases), As (0.005, 0.003 mg.l^{-1} and bd), Ba (0.08, 0.06 and 0.1mg.l^{-1}), Sr (3, 3 and 4 mg.l^{-1}), Zn (bd in all cases), Cr (bd in all cases), Cu (bd in all cases), Ni (0.06, bd and bd), Cd (bd in all cases), Co (0.04 mg.l^{-1}, bd, bd) and Pb (bd in all cases). In all the cases, AMD treatment by the applied doses of biomass ash was effective. In addition, there was no harm caused to the environment since the technology didn't involve any release of hazardous elements from the used ash samples into the aqueous medium.

Key words: acid mine drainage (AMD), biomass ash, treatment, pH, metals.
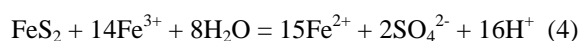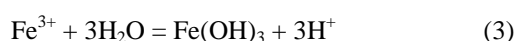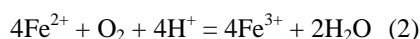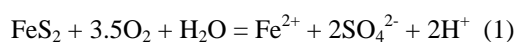
1. INTRODUCTION

The issue of mine waters has lately been extremely topical as various technologies for mine water treatment are being developed with regard to stricter environmental requirements and regulations. Apart from the traditional procedures of alkalinisation by lime, limestone, sodium hydroxide or calcium hydroxide, new initiatives appear searching for cheaper and more effective neutralization agents (Gitari et al., 2008). Some of them consider utilizing certain industrial wastes, e.g.

dust from cement plants, waste from bauxite refining in aluminium production (Doye & Duchesne, 2003), blast furnace slag (Ziemkiewicz & Simmons, 2003) or coal fly ash (Gitari et al., 2008).

Mine waters - classification of mine waters (further referred to as MW) as for their chemical composition is difficult. There are numerous classification schemes based on one or several MW parameters, e.g. content of major cations and anions. Next, it is possible to classify MW according to the pH value (Morin & Hutt, 2010), pH value and concentration of Fe^{2+} and Fe^{3+}, pH value and total

dissolved metal content, etc. (Ficklin et al., 1992). From the point of view of composition and related environmental impacts, the most troublesome is acid mine drainage (AMD), which forms through the oxidation of sulphidic minerals (Stumbea, 2010; 2013). During the oxidation of sulphidic minerals, free acid is formed, and metals and sulphates are released into water, which accelerates leaching of other elements from waste rock. This results in AMD containing sulphates, heavy metals (Fe, Cu, Pb, Zn, Cd, Co, Cr, Ni, Hg), semi-metals (As, Sb) and other elements (Al, Mn, Si, Ca, Na, K, Mg, Ba, F). The major agent which introduces hydrogen ions into MW is the oxidation of pyrite FeS_2 and of other sulphides (sphalerite ZnS, galenite PbS, marcasite FeS_2, etc.) (Lottermoser, 2010). The pyrite oxidation process has been widely studied and it may be summarized into the following reactions below (1) – (4).

$$FeS_2 + 3.5O_2 + H_2O = Fe^{2+} + 2SO_4^{2-} + 2H^+ \quad (1)$$

$$4Fe^{2+} + O_2 + 4H^+ = 4Fe^{3+} + 2H_2O \quad (2)$$

$$Fe^{3+} + 3H_2O = Fe(OH)_3 + 3H^+ \quad (3)$$

$$FeS_2 + 14Fe^{3+} + 8H_2O = 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \quad (4)$$

First, pyrite is oxidized by oxygen in the presence of water, and Fe^{2+}, sulphates and H^+ ions are formed (1). The second step lies in the oxidation of Fe^{2+} to Fe^{3+} reaction (2), which may be catalyzed by the bacteria of *Acidithiobacillus ferrooxidans*. This reaction is usually the limiting factor in the formation rate of acid waters. Other processes depend on the water's pH value. If pH > 3.0, ferric hydroxide precipitates (3). However, if pH < 3.0 and Fe^{3+} gets in contact with oxygen-free pyrite, then it is used up in the oxidation of pyrite (4) as Fe^{3+} is a strong oxidant (Ríos et al., 2008; Šráček, 1997).

The methods of MW treatment may be divided into active and passive ones. All of them make use of various physical, chemical and biological procedures to lower the concentrations of undesirable substances (Luptáková et al., 2012). Active methods require a continuous supply of reagents, active maintenance and monitoring, and make use of mechanical agitators to stir the reagents into the mine water. Passive methods exploit the natural water flow, chemical and biological processes; they take place in wetlands, bioreactors, or oxic or anoxic limestone beds (Lottermoser, 2010). There are also alternative active mine water treatment methods, such as biodesalination process, which combines the treatment of mine waters and sewage waters (Černík, 2008).

Both the passive and active methods of mine water treatment are well examined. Nevertheless, alternative materials, which would reduce the costs of mine water treatment, are still searched for. The subject of numerous studies is the application of coal fly ash as a neutralization agent in AMD treatment. The studies have observed various parameters, such as monitoring of mineral phase dissolution from the fly ash and its reactions with metals contained in mine water (Gitari, 2008). Authors in India observed a reduction in mine water hardness by means of modified fly ash (Prasad et al., 2011). Mine water treatment using synthetic zeolites from coal fly also proved as effective, especially in metal elimination (Gitari, 2005).

Biomass ash - Among renewable resources, biomass is considered the most prospective energy resource (Kalembkiewicz & Chmielarz, 2012). At present combustion of biomass is supported world-wide. In total about 95–97% of the world's bioenergy is produced by direct combustion of biomass (Vassilev et al., 2013). Its primary advantage is its renewability as well as low harmful emission values (Li et al., 2012). The final product of biomass combustion is ash. Considering the fact that biomass combustion is gaining on importance in the energy industry, there is also a rise in the production of biomass ash (Vassilev et al., 2013).

Ash belongs among wastes considered as 'energy by-products'. The composition of biomass ash (further referred to as BA) depends on a number of factors. Its properties and composition vary in dependence on the type of plants, their origin, plant parts (e.g. bark, wood, stumps), the course of the combustion process, temperature, or co-combustion with other fuel types. They also depend on the technology of dust particle separation and the storing method post combustion. With regard to those factors, ashes differ in their chemical and physical properties (Isnam & Knapp, 2011; Vassilev et al., 2010).

During the combustion process, organic carbon is largely oxidized, nitrogen liberates in the form of gas products, and the majority of other elements abundant in the plant material remain in the ash. Ash from wood combustion mostly contains Ca, K, Mg, Si, Al, P, Na, Mn and S. There are traces of Fe, Zn, As, Ni, Cr, Pb, Cu, Hg, B, Mo, Ba, V, and Cd; their abundances vary in dependence on the plant type (Isnam & Knapp, 2011; Váňa, 2010).

Fly ash and slags may be utilized in the building industry in the production of concrete and mortar, where slags and scoria function as aggregates. Next, they may function as aggregates for cement, bricks, or artificial aggregates, and may

be added into asphalt. Fly ash may be used in hazardous waste disposal via its solidification. Next, another application option is in waste water treatment where the ash may be used to produce waste water treatment filter fillings for the elimination of phenols, cyanide, pesticides, mercaptans, etc. (Fiedor, 2012). In addition, biomass ash can be used as a fertilizer. However, the amount of heavy metals contained in the ash may pose problems (Isnam & Knapp, 2011). Another complication of BA as fertilizers lies in its dusting. Ash from biomass combustion may thus be co-applied with farm fertilizers, such as manure or liquid manure (Váňa, 2010).

The objective of the experiment is to examine the effects of biomass ash on the composition of mine water. First, alkalinisation properties of BA and changes in pH in dependence on its dose are tested. Based on the measured results, three BA doses vital to reach the pH value of 8, 10 and 12 are selected. After the treatment of AMD samples using the required doses to reach pH of 8, 10 and 12, were in the individual experiments observed changes in the pH value and turbidity for 7 days long period. The samples were analysed for metal contents, which had been abundant either in AMD or ash, or in AMD and ash simultaneously, in selected times of occurrence of the changes in pH and turbidity.

2. MATERIALS AND METHODS

2.1. Sampling sites

Wood ash sample - biomass ash from Hodonín Power Plant, Czech Republic, was used. The sample was drawn in August 2012. At the time of sampling, only wooden chips were used for combustion as the earlier experience had proved that the combustion of other types of phytomass loads the boilers. It was the case of a fluid ash sample from electric separators. The sample was kept air sealed to prevent oxidation of unstable mineral phases. The properties of the drawn ash sample were analyzed in the Centre of Nanotechnologies of VŠB – TU Ostrava. The total elemental analysis of biomass ash was executed on powder briquettes by X-ray fluorescence (XRFS) and reported in wt. % for oxides and mg.kg^{-1} for trace elements. All the analyses were carried out using a SPECTRO X-LAB spectrometer. Next, specific surface was identified by BET adsorption isotherm with the use of SORPTOMATIC 1990 machine. The grain size of the used ash was < 1 mm.

AMD sample - AMD was drawn on September 2012 from the Jiří open cast at the Sokolov deposit that is under the control of the Sokolovská uhelná, právni nástupce a.s.. This company is the smallest brown coal mining company in the Czech Republic. Currently, mining is executed in two open casts. In the locality mine waters are pumped into the mine water treatment plant, including aeration and alkalinisation, followed by sludge separation. AMD analysis was carried out in the Central Laboratories of the company Aqualia infraestructuras inženýring (Ostrava, CZ).

2.2. Batch experiments

First, changes in the pH value were observed in dependence on the ash dose. In each experiment, one litre of mine water and a dose of ash (batches of 1-22 g of BA) were agitated in a mechanically-agitated column MK6 at 150 rev. min^{-1} for 10 minutes. Next, the samples were filtered using a filter paper for a qualitative analysis (KA 4 filter - speed medium fast) and in the filtrate the pH value was measured. The read values served to decide on BA batches to reach suitable pH in AMD, i.e. about 8, 10 and 12. The BA doses were further used in experiments focusing on the study of mine water after mutual interaction. Contact times were subsequently selected as 1, 5, 30, 60, 360, 720, 1440, 2880, 7200 and 10080 minutes of agitation of BA and AMD. For contact times 1 and 5 minutes, agitation took place in the mechanically-agitated column MK6 at 150 rev. min^{-1}; for the contact times of 30, 60 and 360 minutes agitation in the mechanically-agitated column MK6 started at 150 rev. min^{-1} for the first 10 minutes, and then the speed was reduced to 50 rev. min^{-1}; for the contact times of 720, 1440, 2880, 7200 and 10080 minutes the magnetic mixer LAVAT MM4 was used for agitation and the beakers containing the suspension were covered up with a parafilm in order to prevent evaporation of the samples.

All the batches were tested in three identical experiments. In the first case, having completed the selected contact time, the samples were filtered using a filter paper for a qualitative analysis (KA 4 filter - speed medium fast) and the pH value was determined using a pH/mV Pocket Meter WTW pH 330i in the filtrate. In the second and third cases, after 10-minute or 30-minute sedimentation, turbidity was measured in the non-filtered, settled sample in a measuring cylinder using a turbidimeter HACH 2100Qis. Based on the metered results, times of the occurrence of changes in pH and turbidity were selected, and for the relevant cases the filtrate underwent chemical analyses. The following metal concentrations in the filtrate were observed, namely

Na, K, Mg, Ca, Fe, Mn, Al, Zn, Ba, Sr, Cd, Cu, Co, Cr, Pb and Ni. The metal content had to be assessed with respect to their occurrence in the used AMD and biomass ash. The analyses of raw and treated AMD were carried out as follows: determination of Na, K, Mg, Ca, Mn, Ni, Cd, Co, Cu, Cr, Fe, Zn and Pb using the method of flame AAS (Varian AA 280FS); determination of Al, Ba, Sr and V using the method of ICP-AES (SPECTRO VISION EOP); to determine As the method of electrothermal AAS was used; Hg was determined by an AMA 254 analyser. The AMD had over-limit concentrations of SO_4^{2-}. Sulphates were determined using pre-programmed methods HACH No. 995 at a wavelength of 450 nm on a spectrophotometer HACH DR/2000 (Direct reading spectrophotometer) using reagent SulphaVer 4, which contains $C_6H_8O_7$ and $BaCl_2$.

3. RESULTS AND DISCUSSION

3.1. Chemical composition of BA and AMD

Sample of used biomass ash contains high concentration of main oxides and some trace elements (Table 1). Dominant components are SiO_2 (45.4 wt.%), CaO (17.8 wt. %), Al_2O_3 (13.4 wt. %) and Fe_2O_3 (4.12 wt.%). From trace elements is significant content of Ba (961 mg.kg^{-1}), Zn (524 mg.kg^{-1}), Sr (367 mg.kg^{-1}), Cu (123 mg.kg^{-1}) and Pb (115 mg.kg^{-1}). Value of the biomass ash specific surface is 4.47 m^2.g^{-1}.

Table 1. Chemical composition of biomas ash (oxides [wt. %], elements [mg.kg^{-1}])

Oxides	wt. %	Elements	mg.kg^{-1}
Na$_2$O	< 1	Ni	25
MgO	6	Cu	123
Al$_2$O$_3$	13.4	Zn	524
SiO$_2$	45.4	As	13
P$_2$O$_5$	2.1	Rb	106
SO$_3$	3.14	Sr	367
K$_2$O	3.11	Mo	< 3
CaO	17.8	Cd	7.2
TiO$_2$	0.72	Cs	< 3
MnO	0.57	Ba	961
Fe$_2$O$_3$	4.12	Hg	< 4
		Pb	115
		Cl	0.46
		V	< 35
		Cr	68
		Co	< 25

Mine water sample used for treatment experiments is characteristic by high concentration of SO_4^{2-}, Ca, Mg, Na, Al, Mn and Fe (Table 2). Turbidity of raw mine water sample is 0.8 FNU.

3.2. Variation in pH at different biomass ash doses

The pH value of the raw AMD sample is 2.7. To start with, alkalinisation properties of the biomass ash were assessed when in contact with AMD. The dependence of pH on the biomass ash dose (Fig. 1) implies that to reach pH 8 the required biomass ash dose was 2.9 g.l^{-1}, for pH 10 it was 6 g.l^{-1} and for pH 12 the dose of BA was 20 g.l^{-1}.

Table 2. Initial chemical analyses of mine water [mg.l^{-1}]

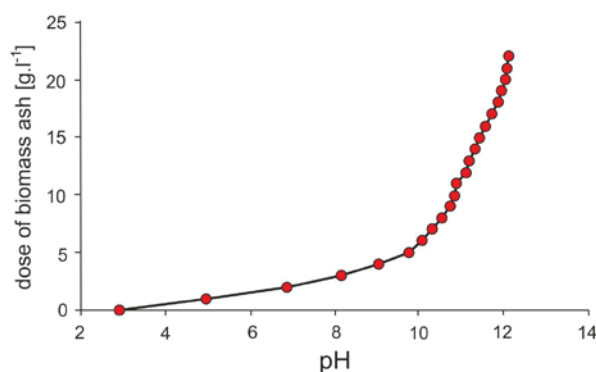| Indicator	mg.l^{-1}	Indicator	mg.l^{-1}
Ca	265.52	Ni	0.27
Mg	96.62	Pb	< 0.005
Fe	20	Cd	< 0.001
Mn	5.17	K	9.7
Al	15.15	Co	0.18
Na	202	Ba	0.04
Zn	0.76	As	0.0025
Cu	0.12	Sr	2.6
Cr	< 0.001	SO$_4^{2-}$	1576

Figure 1. Graph of correlation between pH values of tested water and the dose of biomass ash [g.l^{-1}]
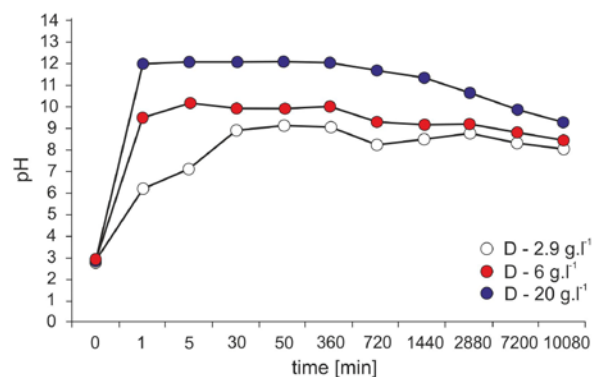

Figure 2. Development of filtrate pH in dependence on time for ash doses of 2.9 g; 6 g and 20 g.

Figure 2 gives a graphic representation of the dependence of the development of AMD pH values at the reaction time at selected biomass ash doses. The top ash dose of 20 g shows an almost immediate rise in pH to 12.1 in the treated AMD. This value does not change much up to the 360th minute of the reaction; since 720th minute a gradual fall can be observed. As for the lowest BA dose of 2.9 g, there is a gradual increase in pH of the treated AMD and it levels off after 30 minutes of the reaction. After 720 minutes the pH values drop in all the BA doses. At the end of the experiment, in 1 l of AMD and 20 g/ 6 g/ 2.9 g of biomass ash the pH value was 9.3, 8.5 and 8.2 respectively. The slower increase in pH in the case of the lowest ash dose may be attributed to a gradual hydrolysis of Fe^{3+}, Fe^{2+}, Al^{3+} and Mn^{2+}, during which H^+ ions release (Gitari, 2008). In the top ash dose, the highest pH is achieved instantly, which points at the dominant role of the excess of alkalis.

3.3. Turbidity

For the purposes of the study, turbidity was observed as a fast indicator of changes in the treated water chemical composition during the mutual interaction of biomass ash and AMD. During the experiments selected doses of BA were used, namely 2.9 g, 6 g and 20 g, each with 1 litre of AMD. The variations in turbidity in the settled samples (after 10-minute sludge sedimentation and after 30-minute sludge sedimentation) occurred at the time interval of 30 min (Figs. 3 and 4). This value was the lowest of all values measured during the overall experiment even if turbidity dropped having added all the three biomass ash doses. In addition, at the time of 720 min there was a fast increase of turbidity, and at the time of 1440 min there was a rapid decrease of turbidity (Figs. 3 and 4).
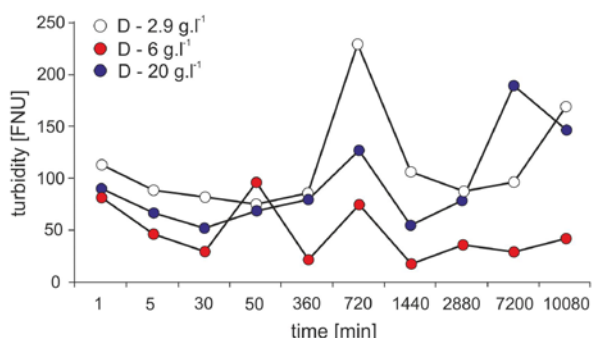

Figure 3. Development of turbidity in time after 10-minute sludge sedimentation

Further to the measured results, times of changes in turbidity or pH were identified, specifically at 30, 720, 1440 and 10080 minutes. Having analysed the filtrate, the measured results were compared with the legal requirements valid for the Czech Republic (Government Order No. 61/2003 Coll.; Pitter, 2009).
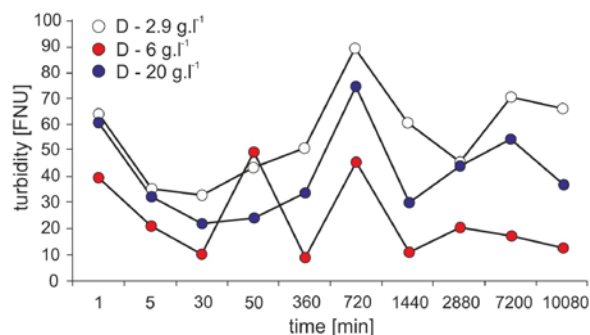

Figure 4. Development of turbidity in time after 30-minute sludge sedimentation

3.4. Batch experiments

Calcium - content of CaO in the biomass ash was 17.8 wt. %. In the mine water the initial concentration of Ca was 265.52 mg.l⁻¹. Having added the BA, there was a significant increase in Ca concentration in MW, where at the start of the experiment we may observe a rise in the concentration of Ca along with an increase in BA (Fig. 5a). On the contrary, in the course of the experiment the most prominent drop in the concentration of Ca in the filtrate was when the dose of BA was the highest, i.e. 20 g.l⁻¹, followed by the doses of 6 g.l⁻¹ and finally 2.9 g.l⁻¹. This course may be attributed to Ca precipitation, predominantly in the form of $CaCO_3$. The efficiency of Ca precipitation rises along with its concentration in the solution. At the lowest dose the concentration hardly changes. At the end of the experiment, the Ca concentration using 1 l of AMD and 2.9 g of BA was 448.47 mg.l⁻¹ of Ca, using 6 g of BA it was 422.18 mg.l⁻¹ of Ca and using 20 g of BA it was 376.27 mg.l⁻¹ of Ca. The limit for Ca is 190mg.l⁻¹ (Pitter, 2009). During the experiments using all the doses, the concentration of Ca in AMD was higher than the limit mentioned above. In all the BA doses it is possible to observe variations in the concentration of Ca in time. Using the top ash dose, i.e. 20g, the concentration of Ca falls in time after the initial increase; in other doses it does not change significantly.

Magnesium - content of MgO in the biomass ash was 6 wt. %. The initial concentration of Mg in the mine water was 96.62 mg.l⁻¹. In the course of the experiment, Mg was eliminated only when the top BA dose was applied, i.e. 20 g (Fig. 5b). Using the

dose of 2.9 g of BA there was a rise in the concentration of Mg in AMD, which increases along with time. This means that Mg liberates from the biomass ash into the solution. As for the doses of 6g of BA and 20 g of BA the concentration of Mg ions dropped; in the case of the dose of 20 g, the value almost drops to zero. This course may be attributed to the pH value as to remove Mg in water technology precipitation of Mg ions into $Mg(OH)_2$ is used at the pH value over 9 (Pitter, 2009). After 10080 minutes (7 days) the doses are observed for a slight increase in the concentration, which may be associated with a decrease in pH. The abundance of Mg ions in the filtrate thus depends on the pH value. At the end of the experiment, i.e. after seven days, the concentration of Mg in solution after using the biomass ash dose of 2.9g was 134.67 mg.l^{-1} of Mg, using 6 g of BA it was 81.90 mg.l^{-1} of Mg and using 20 g of BA it was 7.07 mg.l^{-1} of Mg. In accordance with Government Order No. 61/2003 Coll. as amended, the limit for magnesium is 120mg.l^{-1}. The initial value of Mg concentration in the MW was acceptable (Table 2), in the course of the experiment there was an increase in the concentration of Mg ions having added 2.9 g of BA. The dose of 6 g of BA caused a decrease in the concentration to levels that are admissible subject to the Government Order, and in the top BA dose (20g) the value dropped almost to zero.

Sodium - content of Na_2O in the biomass ash was below the detection limit (< 1 wt. %). Its initial concentration in the mine water was 202.0 mg.l^{-1}. In the majority of cases, the experiment resulted in lower concentrations of Na in AMD (Fig. 5c) as again there were variations in the Na concentrations in the filtrate depending on the contact time. The concentration of Na is not limited for surface or ground water, however, there is a limit value for drinking water and hot water subject to Regulation 252/2004 Coll., regulating sanitary requirements for drinking and hot water and the frequency and extent of drinking water quality checks, as amended in Regulation 187/2005 Coll. and Regulation 293/2006 Coll., i.e. 200 mg.l^{-1}. The abundance of Na in water may further restrict its use, e.g. in irrigation. At the end of the experiment, the concentration of Na in 1 l of treated AMD using 2.9 g of BA was 126.67 mg.l^{-1} of Na, using 6 g of BA it was 123.34 mg.l^{-1} of Na and using 20 g of BA it was 171.81 mg.l^{-1} of Na.

Potassium - content of K_2O in the biomass ash was 3.11 wt. %, and in the MW the initial concentration of K was 9.7 mg.l^{-1}. In all the doses it is possible to observe a gradual increase in the K concentration in MW, both along with time as well as with higher doses, which points at its gradual

release from the ash (Fig. 5d). The abundance of K in water is not significant from the point of view of sanitation, and there is no limit for its concentration in both surface and ground water (Pitter, 2009). At the end of the experiment, the concentration of K using 2.9 g of BA was 13.80 mg.l^{-1} of K, using 6 g of BA it was 21.30 mg.l^{-1} of K and using 20 g of BA it was 53.49 mg.l^{-1} of K.

Iron - content of Fe_2O_3 in the biomass ash was 4.12 wt. %. In the mine water the initial concentration of Fe was determined as 20 mg.l^{-1}. Applying each ash dose significant amounts of Fe were removed from AMD along with time (Fig. 5e). As for all the experiments, the concentration of Fe in the filtrates was below the detection limit. This may be attributed to the precipitation of Fe into the form of its oxides and hydroxides with the rise of pH value of the solution. According to Government Order No. 61/2003 Coll. as amended, the limit for Fe is 0.55 mg.l^{-1} for water supply courses, and the mean value complying with the environmental quality standard is 1 mg.l^{-1} (Pitter, 2009). In the experiment Fe was eliminated from AMD to meet the limit values for water supply courses.

Manganese - content of MnO in the biomass ash was 0.57 wt. %. During the initial analysis of mine water the concentration of Mn was determined as 5.17 mg.l^{-1}. Using each ash dose to treat AMD in the suggested time intervals, Mn was eliminated from AMD. This is to do with its precipitation into the form of its oxides and hydroxides during AMD alkalinisation.

The pH value required to remove Mn should exceed 8.3. (Bindzar, 2009). In accordance with Government Order No. 61/2003 Coll. as amended, the mean value for Mn complying with the environmental quality standard is 0.3 mg.l^{-1}. At the end of the experiment, the concentration of Mn in 1 l of AMD using 2.9 g of BA was 1.37 mg.l^{-1} of Mn, using 6 g of BA it was 0.063 mg.l^{-1} of Mn and using 20 g of BA it was <0.005 mg.l^{-1} of Mn (Fig. 5f). The residual concentration of Mn in the filtrate corresponds to the pH value.

Aluminium - content of Al_2O_3 in the biomass ash was 13.4 wt. %. The concentration of Al in raw AMD was 15.15mg.l^{-1}. In the course of the experiment, a significant decrease in Al concentration can be observed with all the used BA doses in time (Fig. 5g). During hydrolysis of Al ions hydroxocomplexes are formed. Important are also polymer reactions, during which various polynuclear hydroxoaluminates arise which may have a colloid character. Gradually, a solid phase forms, i.e. hydrated aluminium oxide $Al_2O_3.xH_2O$ (also amorphous $Al(OH)_3$), whose composition varies and changes with time.
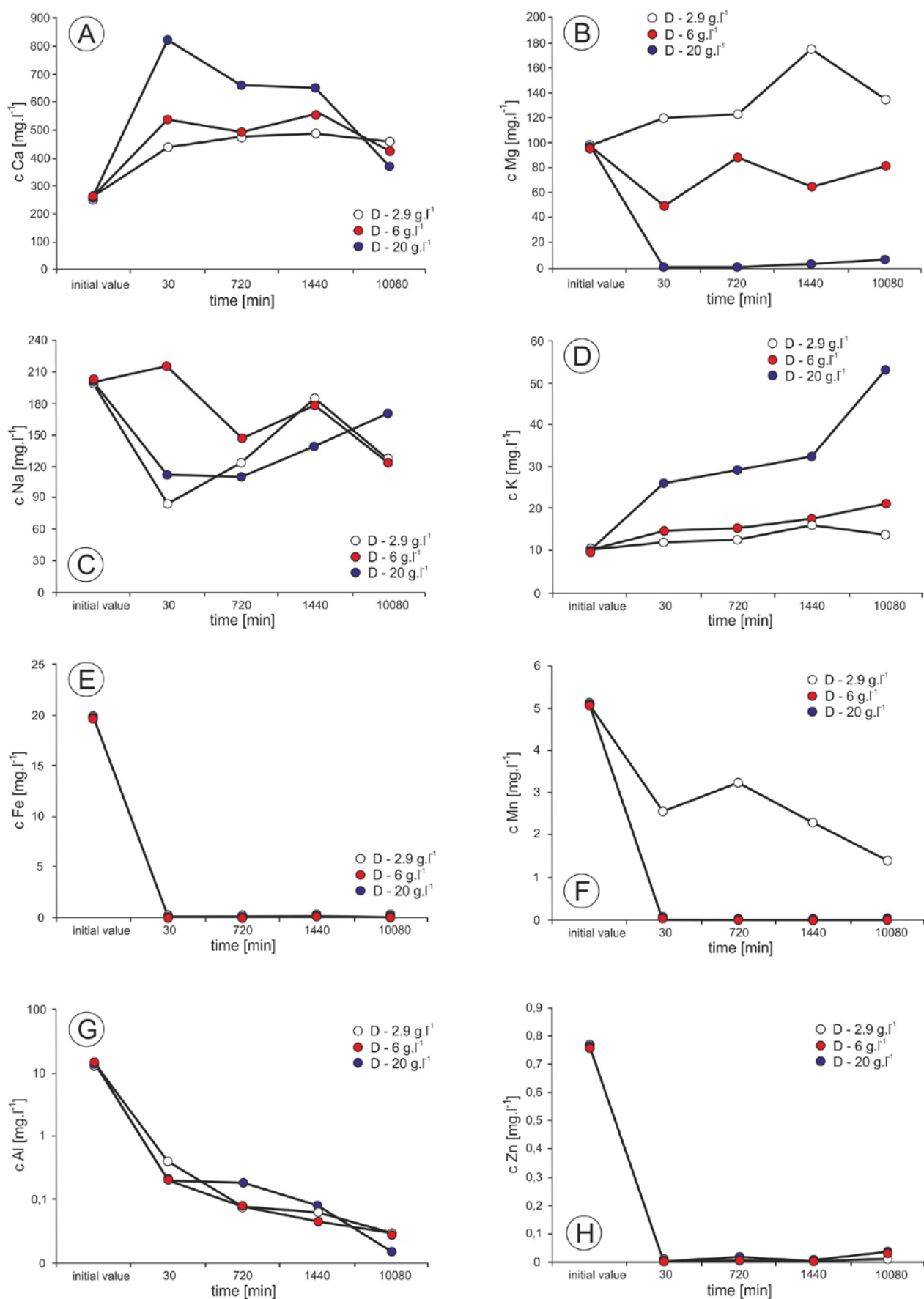
Figure 5. Graph of correlation between concentration of observed elements in filtrate and reaction time A) Ca; B); Mg; C) Na; D) K; E) Fe; F) Mn; G) Al; H) Zn (mg.l⁻¹), (D – dose of BA)

Due to ageing (already after 6-9 hours) the solid phase crystallizes, and in dependence on the conditions either $AlO(OH)$ or $Al(OH)_3$ arise. Those modifications are exploited in water technology as adsorption agents (Pitter, 2009). Subject to Government Order No. 61/2003 Coll. as amended, the limit value for Al was 0.45 $mg.l^{-1}$ for water supply courses, and the mean value complying with the environmental quality standard (1 $mg.l^{-1}$). The concentration of Al in the filtrate was below 0.45 $mg.l^{-1}$ already after 30 minutes. At the end of the experiment, i.e. after the seven-day interaction, in the case of all the ash doses the concentration of Al is below the detection limit (Fig. 5g).

Zinc - content of Zn in the biomass ash was 524 $mg.kg^{-1}$. The concentration of Zn in raw AMD was 0.76 $mg.l^{-1}$. All the BA doses in the observed time intervals have cost decrease of the Zn concentration in treated AMD. Applying the doses from 2.9 g to 20 g of BA, Zn was removed all the way below the detection limit in almost all observed time intervals (Fig. 5h). The mechanism of Zn removal is predominantly precipitation into the $Zn(OH)_2$ (solid phase) at pH value over 8 (Pitter, 2009). Subject to Government Order No. 61/2003 Coll. as amended, the limit value for Zn is 0.092 $mg.l^{-1}$ as the mean value complying with the environmental quality standard. During the experiment, content of Zn in filtrate was reduced all the way to the value required by law using each ash dose in all the observed time intervals.

Arsenic - content of As in the biomass ash was 13.4 $mg.kg^{-1}$. The mine water was studied for the initial concentration of As, which was 0.0025 $mg.l^{-1}$. Arsenic is rather mobile in the aqueous medium. It may form low-soluble arsenates of various metals, it has a considerable capacity of accumulation in the sediment, and adsorption to and co-precipitation with iron hydroxides and aluminium hydroxides have been proved (Pitter, 2009; Lottermoser, 2010; Carlson et al., 2002). On the other hand, due to changes in pH and reduction potential, desorption may occur, while As competes for adsorption sites with sulphate ions (Carlson et al., 2002); due to the dissolution of minerals containing As, either primarily combined or due to co-precipitation, it may liberate back into the aqueous medium (Lottermoser, 2010). In the case of some experiments there was a slight increase in the concentration of As in the solution of mine water and BA (Fig. 6). In the case of the medium and lowest doses of BA (i.e. 6g and 2.9g respectively) the concentration of As fluctuates. The maximum was achieved after 12 hours (720 minutes) of the reaction, namely 0.0048mg.l^{-1} and 0.0032 mg.l^{-1}

respectively. This maximum corresponds to the maximum value of turbidity. In the case of the top BA dose (20 g) the concentration of As in all the observed time intervals was below the detection limit (Fig. 6). The limit value for As is 0.005 $mg.l^{-1}$ for water supply courses, and the mean value complying with the environmental quality standard is 0.011 $mg.l^{-1}$ (Pitter, 2009). Carrying out all the experiments no limits for water supply courses were exceeded.
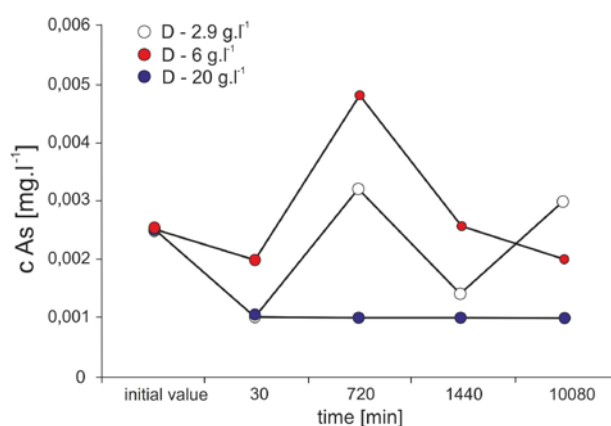

Figure 6. The graph of correlation between concentration of As ($mg.l^{-1}$) in filtrate and the reaction time (D - dose of BA)

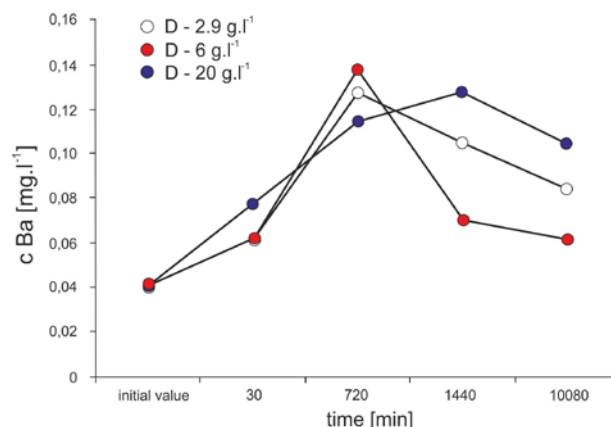Figure 7. The graph of correlation between concentration of Ba ($mg.l^{-1}$) in filtrate and the reaction time (D – dose of BA)

Barium - content of Ba in the biomass ash was 961 $mg.kg^{-1}$. The initial concentration of Ba in the mine water was 0.04 $mg.l^{-1}$. In all the ash doses and each observed time intervals there was a slight increase in concentration of Ba in the filtrate when compared with the initial concentration in AMD (Fig. 7). The variations in the concentration of Ba in time; for doses of 2.9 g and 6g of BA the Ba concentration reaches its maximum after 12 hours, i.e. the values of 0.128 $mg.l^{-1}$ of Ba and 0.138 $mg.l^{-1}$ of Ba respectively. In the case of the top ash dose,

the maximum concentration after 24 hours is 0.128 mg.l^{-1} of Ba, and then the concentrations levels drop for all the ash doses (Fig. 7). For the removal of Ba from water, the formation of low-soluble $BaSO_{4(s)}$ is significant (Pitter, 2009). At the end of the experiment, the concentration of Ba using 2.9 g of BA was 0.084 mg.l^{-1} of Ba, using 6 g of BA it was 0.061 mg.l^{-1} of Ba and using 20 g of BA it was 0.104 mg.l^{-1} of Ba. In accordance with Government Order No. 61/2003 Coll. as amended, the limit value for Ba is 0.18 mg.l^{-1} as the mean value complying with the environmental quality standard. In the course of all the carried out experiments this limit concentration was not exceeded in any sample.

Strontium - content of Sr in the biomass ash was 367 mg.kg^{-1}. In the mine water the initial concentration of Sr was determined as 2.6 mg.l^{-1}. There was a rise in the concentration of Sr in AMD having added each dose of BA in all the observed time intervals (Fig. 8). Nevertheless, Sr is not toxic and it is common in natural water. Strontium is not limited in any water types (except for the radionuclide ^{90}Sr) in Czech republic (Pitter, 2009). At the end of the experiment, the concentration of Sr in 1 l of the treated AMD using 2.9 g of BA was 3.2 mg.l^{-1} of Sr, using 6 g of BA it was 3.3 mg.l^{-1} of Sr and using 20 g of BA it was 3.83 mg.l^{-1} of Sr.
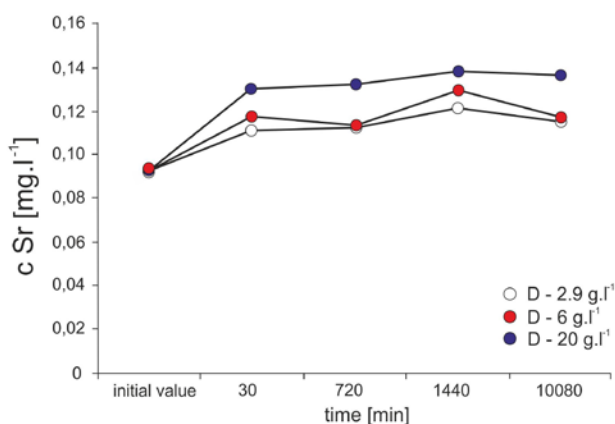

Figure 8. The graph of correlation between concentration of Sr (mg.l^{-1}) in filtrate and the reaction time (D – dose of BA)

Chromium, copper, nickel, lead, cadmium, cobalt and sulphates - in the next stage of experiments, metals amounting to hundredths or thousandths of mg.l^{-1} in AMD were observed as well as trace elements were determined in the biomass ash, i.e. those in units of mg.kg^{-1}. To start with Cr, in the mine water the initial concentration was below the detection limit and the concentration in the BA was 68 mg.kg^{-1}. Cr^{3+} ions more easily succumb to hydrolysis under the formation of $Cr(OH)_{3(s)}$. Another important characteristic of Cr is its adsorption onto

hydrated oxides of Fe, Mn, and Al, especially in an alkaline medium (Pitter, 2009). The limit set by law for water courses is 0.018 mg.l^{-1} of Cr.

The initial concentration of Cu in the mine water was 0.12 mg.l^{-1}, and in BA it was 123 mg.kg^{-1}. In neutral and alkaline ranges (which are considered within our experiment) solubility of Cu is limited by the solubility of $Cu(OH)_{2(s)}$ (at pH 8-12 its solubility is in the order of hundredths of mg.l^{-1}); if sulphides are present, SO_4^{2-} comes into question; if SO_4^{2-} is present, then $Cu_3(OH)_4SO_{4(s)}$ or $Cu(OH)_6SO_{4(s)}$ can be considered (Pitter, 2009). For water courses the limit set by law is 0.014 mg.l^{-1} of Cu.

The initial concentration of Ni in MW was 0.27 mg.l^{-1} and in BA the concentration of Ni was 25 mg.kg^{-1}. Nickel can be removed from water as an insoluble hydroxide $Ni(OH)_{2(s)}$; if carbonates are present, then $NiCO_{3(s)}$ is an option; in the presence of sulphides, a sulphide $NiS_{(S)}$ comes into question (Pitter, 2009). The limit set for water courses is 0.020 mg.l^{-1} of Ni.

In the mine water the initial concentration of Pb was below the detection limit, whereas in BA it was 115 mg.kg^{-1}. Lead has a high accumulation index, and thus its sorption onto a solid phase is important when to be removed (Pitter, 2009). The limit set by law for water courses is 0.0072 mg.l^{-1} of Pb.

The initial concentration of Cd in the mine water was below the detection limit; in BA teh concentration of Cd was 7.2 mg.kg^{-1}. In the elimination of Cd from water, precipitation processes (e.g. in the form of hydroxides, carbonates or sulphides) or adsorption are exploited (Pitter, 2009). For water courses the limit set by law is 0.0003 mg.l^{-1} of Cd.

In the mine water the initial concentration of Co was 0.18 mg.l^{-1}, and in the BA it was <25 mg.kg^{-1}. Cobalt may be removed from water as an insoluble hydroxide $Co(OH)_{2(s)}$; in the presence of carbonates - $CoCO_{3(s)}$ is an option; or in the form of sulphide $CoS_{(S)}$ (Pitter, 2009). The limit set law for water courses is 0.003 mg.l^{-1} of Co.

Treating AMD using even the lowest dose of BA (2.9g) it is possible to observe a decrease in the concentration of the majority of metals (except for Ni and Co) all the way below the detection limit (Table 3). Nevertheless, even in the case of nickel and cobalt their concentrations in AMD go down.

Using the medium and top BA doses, i.e. 6 g and 20 g respectively, the concentrations of all the observed metals were below the detection limit in all the set time intervals. As for Cu, Ni and Co, which were abundant both in AMD and BA, their removal from AMD may be greatly attributed to the attained

pH value ranging between 9 and 12 approximately. At such pH values precipitation into the form of hydroxides occurs. Moreover, various amorphous phases arise, onto which the metals may adsorb. At the same time, it may be stated that they do not mobilise from BA into AMD. As for Pb, Cd and Cr, we may also claim that their mobilisation from BA into the aqueous medium using the stated BA doses does not take place.

Table 3. Concentration of trace elements in treated water after use of 2.9 g.l^{-1} of biomass ash

Time	pH	Turbidity	Cr	Cu	Ni	Pb	Cd	Co
min		FNU			mg.l^{-1}			
0	2.87	0.8	bd	0.12	0.27	bd	bd	0.18
30	8.95	32.6	bd	bd	0.11	bd	bd	0.07
720	8.27	91	bd	bd	0.15	bd	bd	0.13
1440	8.52	60.9	bd	bd	0.14	bd	bd	0.06
10080	8.21	66.3	bd	bd	0.06	bd	bd	0.04

From anions, the treated AMD was only studied for the concentration of SO_4^{2-}. Initial concentration of SO_4^{2-} in the mine water was 1579.8 mg.l^{-1}. The content of SO_3 in the biomass ash was 3.14 wt. %. In all the experiments, the concentration of SO_4^{2-} ions ranged from 1516 mg.l^{-1} to 1608.2 mg.l^{-1}. The results confirm the hypothesis that treating AMD using biomass ash, SO_4^{2-} in AMD are not removed or their concentrations are not increased either.

4. CONCLUSIONS

The purpose of this study was to examine the effect of biomass ash (BA) on the composition of acid mine drainage in their mutual interaction. The composition of the BA is ideally preconditioned to be used in AMD treatment. Nevertheless, BA also contains hazardous elements and, thus, it is important to consider their potential mobilisation into AMD. In dependence of pH in AMD on the dose of biomass ash, three doses of BA were selected, during which the pH values of 8, 10 and 12 in AMD were obtained after 10-minute agitation and using 2.9 g, 6 g and 20 g of biomass ash. The doses were agitated along with AMD for 7 days, while the values of pH and turbidity were observed. In selected time intervals when changes occurred in pH and turbidity, the samples were analysed for their metal content. Examined were metals which were abundant in MW or BA at the start of the experiment. Based on the measured values, it may be stated that depending on its content of alkalis the

biomass ash has the capacity to increase pH in AMD, all the way to the very alkaline range. The abundance of all the observed elements in the filtrates within all the experiments largely depends on the pH value.

In the case of Ca and K, their concentrations increased in AMD in all the tested batches. Using the top BA dose, Mg is removed from AMD with an almost 100% efficiency; using the lowest dose, the concentration rises and in the case of the medium BA dose, the Mg concentration in AMD was reduced by about 8% to 48% depending on the pH value or the contact time of BA and AMD. With the exception of one experiment, the concentration of Na is lower than its initial content in AMD. The concentration of Na in the treated AMD varies irregularly in time and amount of BA dose.
Iron is removed almost instantly with an almost 100% efficiency using all the doses of BA. Manganese was removed from the samples using the top and medium ash doses; in the lowest dose the removal efficiency of Mn from AMD was from 37% to 73% in dependence on the pH value or the contact time of BA and AMD.

In the case of Al, the concentration decreased gradually in time. After seven days the concentration of Al was below the detection limit in all the samples. In the course of the reaction, Zb was almost entirely eliminated from AMD using all the biomass ash doses.

Arsenic, Ba and Sr were partially mobilise from BA, however, the extent of their mobilisation is not such to exceed the values meeting the environmental quality standard or the limit values for water supply courses subject to valid legislation.

The concentrations of Cr, Cu, Nil, Cd, Co and Pb in AMD were below the detection limit using the BA doses of 6g and 20g in all the observed time intervals. In the case of the lowest dose, Cr, Cu, Cd and Pb were also below the detection limit, with the exception of Ni and Co, whose initial concentration in AMD was reduced from 39% to 76% for Ni and from 28% to 78% for Co, in dependence on the pH value or the contact time of BA and AMD.

In AMD treated by the biomass ash doses there is an over-limit residual concentration of sulphates and alkali metals. Nevertheless, using standard neutralizing agents their concentrations are similarly excessive.

Acid mine drainage treatment using biomass ash is very effective and comparable to commercially available agents. At the same time, the mobilisation of hazardous elements from biomass ash is negligible.

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