Neutralization of Acid Mine Drainage with Wood Ash

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The paper presents the research activities oriented to solving two environmental issues of concern: acid mine drainage that poses a great risk to soils and water, and wood ash disposal, which can be done only under strict conditions, with high costs. After trials with synthetic acid waters, the behavior of four types of ash has been investigated. The ashes used were originated from two boilers belonging to a fiberboard manufacturer, individually and mixed according to their production process, using acid mine drainage from a copper mine. Acid mine drainage has been characterized in what concern pH, fix and mineral residues, as well as Fe, Cu, Zn and Mn content. For all ashes and their mixtures, the pH (water suspension 1:5), humidity, as well as their neutralization capacity have been determined. The obtained results have been very good, proving that wood ash has better neutralization capacity than calcium carbonate, thus enabling to pursue and extend the present research work.

Keywords: Wood waste, fly and bottom ash, copper mine, neutralization, heavy metals

The quest of energy sources has led to the reconsideration of *traditional* fuels, such as wood, a renewable resource with multiple uses. Because just burning logs is not a sustainable option on large scale, wood processing companies, where *waste*, such as chips, bark, sawdust, is produced in large amounts, have built large combustion units, where these materials are burn, with direct influence in cost reduction and environment protection [1,2].

Besides the major advantages offered by this approach, a side-effect is the generation of large amounts of alkaline ash which, according to European and Romanian norms and regulations, must be disposed or, if a thorough study confirms its innocuity, used for various purposes.

Although the use of coal combustion ash is very well documented, and its use as concrete additive is gaining momentum [3-5], in what concerns the wood ash use, the research are not so extended, and its large scale application is still on a waiting list. A reason for this situation is, besides the small amount of wood ash, compared to coal, variation in quality, depending on the type of wood [6]. Thus, ash landfilling is the option of choice for the most wood combustion units [7], with detrimental effects on the environment and with increased production costs. On the other hand, mining faces a big challenge, i.e. the presence of acid mine drainage (AMD), a natural phenomenon, posing multiple problems to the environment. AMD waters represent a serious environmental problem, both in active mines and in those in which it was abandoned the metals extraction process, thus constituting a major source of pollution for surface waters [8]. Acidity in AMD is composed of mineral acidity due to the presence of Cu^{2+}, Fe^{2+}, Fe^{3+}, Zn^{2+}, Mn^{2+} and other metals depending on the specific metal sulfide exposed during disturbance, and hydrogen ion acidity. Generally, AMD is characterized by low *p*H and high sulfate and Fe content [9]. Although natural chemical and biological reactions cause some neutralization of acidity and precipitation of metals, this is not enough, and AMD needs additional neutralization, usually with limestone or lime, which are very efficient, but remains quite expensive [10]. Another option for the neutralization of AMD, is the covering mining waste with alkaline material, or creation of alkaline barriers, even if promising, is in an incipient research stage [11].

In this respect, some laboratory determinations have been performed, in order to ascertain the behavior of the ash produced by a Romanian fiberboard company (which generates 20-40 t daily) on acid waters from an open cast copper mine situated in Apuseni Mountains of Romania (fig. 1), in what concerns the amounts of ash required for the neutralization of acid water, and the amount of copper and other metals found in the effluent, too. The distance between the fiberboard manufacturer and the mine is about 100 km, the two places being linked by a good road. A railway connection is also possible.

Fig. 1. Romanian open cast copper mine, Apuseni Mountains

Until now, these acid waters reached the main pond, where are neutralized with hydrated lime and then a natural dilution process takes place.

At discharging into the nearby river, waters from this pond must comply with the Romanian norms and regulations regarding the waters *p*H and the maximum admissible content of metals. This approach, not studied until now in Romania, is been already researched in other countries, as stated in the works of Heviankova, van Eick and Vadapalli [12-14]. This paper continues a previous research work of the authors with similar subject that contains more theoretical issues [15].

Experimental part

Ash originated from a fiberboard manufacturing company situated in Romania, not far Sibiu, which has

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two powerful combustion units, one using wood waste from the medium density fiberboard (MDF) department and the other wood waste from the particleboard (PB) department. In both units, ash is collected at the bottom (bottom ash - BA) and in hydro-cyclones (fly ash - FA). The generated fly ash amount is three times more than bottom ash in both units, but the total amount of ash resulted in each generator is similar. Bottom and fly ash of each unit are stored in the same containers, and when disposed the content of the MDF and PB are mixed. During storage and transport as well as during landfilling the wet ash dries in various degrees, depending on time and temperature. For the research purposed we have started by determining the chemical properties of each of the four ash types, and then we have mixed them as follows (all samples have been dried at 105 °C, for two hours, and their humidity and respective dry-matter content were determined, by weighing before and after drying - SR EN 12048):

a)300 g FA + 100 g BA from MDF unit (MDF-m)

b)300 g FA + 100 g BA from PB unit (PB-m)

c)200 g MDF-m + 200 g PB-m (F-m)

The resulted final mixture (F-m), has a similar composition with the ash as resulted in the combustion and will be disposed.

The results are presented in table 1, as mean of three determinations.

We have used only dry materials considering that is more relevant than using wet ones, because humidity is a changing parameter, depending on the outdoor temperature and the time since collecting.

Because of the paramount importance of the AMD pH, this parameter was thoroughly determined for all the original ashes, as well for the three mixtures, in water suspension (with a 1:5 solid-liquid ratio), according to SR EN 13037. The measurements have been performed using a Hanna Instruments HI 113 pH-meter, with a HI 1131B glass electrode as indicator electrode. These results are also presented in table 1, as the mean of three determinations.

The acid mine drainage pH was determined using the same pH-meter, according to SR ISO 10523. Besides this, the fix residue and total suspensions were determined, as well as the amount of Cu^{2+}, total Fe, Zn^{2+}, Mn^{2+}, using a ContrAA 700 high resolution and continuous source atomic absorption spectrometer, with graphite furnace, manufactured by Analytik Jena, Germany [16]. After neutralization and settling for one hour, the suspension of each sample was filtered and the total amount of the metals of concern has been determined in the supernatant solution. The composition of AMD, before and after neutralization, is presented in table 2, also as mean of three determinations.

In order to determine the neutralization behavior of the ash, it has been performed the neutralization of 100 mL AMD, adding increasing amounts of each type of dried ash and mixtures (prepared as described above), under stirring on a magnetic plate, using a TitroLine easy device, manufactured by Schott Instruments GmbH – Germany.

Results and discussions

As it may be seen from table 1, all ashes are in humid state, which has the drawback of increasing the amount to be transported but, from the environmental point of view is beneficial, the risk of dust generation during handling being very low.

The ash *p*H is strongly alkaline in all cases, this indicating that part of the dissolved metals occurs as basic metal salts, oxides, hydroxides, and/or carbonates. Therefore, the proportions of soluble basic metal salts, oxides, hydroxides, and carbonates in the ashes outweigh the proportion of soluble acid components, and both ashes subsequently generate an alkaline *p*H [17].

The high alkalinity makes all types of ash good candidates for neutralization of acid mine drainage, and

Table 1
DRY MATTER CONTENT AND *p*H OF THE SAMPLES

	MDF-BA	MDF-FA	PB-BA	PB-FA	MDF-m	PB-m	F-m
Dry matter (%)	61.34	69.41	68.22	75.64	66.32	73.01	74.38
pH - H_2O	12.87	10.80	13.11	9.59	12.58	12.85	12.74
Amount of ash for neutralization of 100 mL AMD (g)	21.60	51.40	18.40	73.80	26.40	24.20	24.80

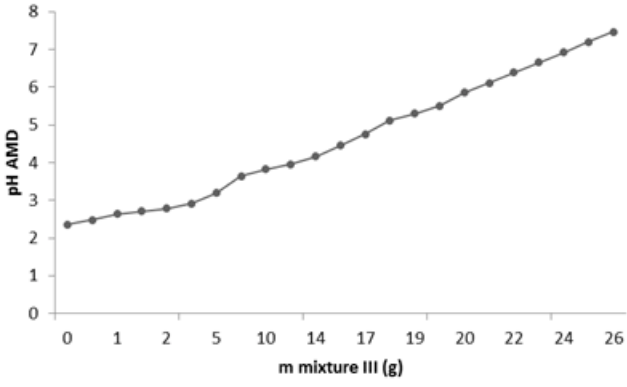

Fig. 2. Neutralization curve for the final mixture

Table 2
ACID MINE DRAINAGE CHARACTERISTICS, BEFORE AND AFTER NEUTRALIZATION WITH THE FINAL ASHES MIXTURE (F-M)

	Fix residue (mg/L)	Total suspensions (mg/L)	Total Fe (mg/L)	Total Cu (mg/L)	Total Zn (mg/L)	Total Mn (mg/L)
Initially (pH = 2.19)	37510	281	2875	495	715	58.40
Finally (pH = 7.195)	1821	92	0.62	0.24	0.17	20.17
Admitted values, according to the operating authorization (pH = 4.7-8.5)	2000	100	30	7.0	3.5	4.0

what is more important, it has been proven that the final mixture of all four types of ashes (F-m) has a good neutralization capacity, i.e. 24.8 g/100 mL AMD, or 248 kg per 1 m^3.

The neutralization curve, for the final mixture is presented in figure 2, with the mention that all the others have similar shapes.

Of course, if it is not intended a full neutralization (*p*H around 7) the process can be stopped earlier, with the subsequent reduction of the amount of ash to be used (for instance, for a *p*H = 5, only 18 g of ash/100 mL AMD is required).

In table 2 there are presented the main parameters of the acid waters, before and after neutralization, together with the maximal admitted values, as defined by the competent authority, to satisfy the environmental authorization for the operation of the company. It is worth to be noted that these values are higher than the national norms, because the volume of AMD is reduced and the impact upon the river it is discharged into is small. On the other hand, these are temporary values, to be revised every year, because the company is going to improve the neutralization system of AMD in order to comply with the Romanian norms and regulations.

As it may be seen from the table 2, the values comply with the operating limits, thus the neutralized AMD could be discharged into the environment. The only major problem is the amount of Mn, which is greater than the admitted value, because of the high amount of Mn in the ash (3170 mg/kg d.w., as determined by AAS).

Being at incipient stage of research, the pursue of activity is required, especially in what the reduction of Mn amount in ash and in water, as well for the practical use of ash, i.e. in neutralizing facilities, as cover for sterile landfills, or others.

Conclusions

The purpose of this study was to determine the acid mine drainage (AMD) neutralization capacity of certain types of wood ash, in the original collecting state and of their respective mixture, considering also the technology and the way they are stored and shipped. The initial types of ash differ largely in *p*H, and this is also reflected in the neutralization capacity of their mixture. The results have shown that bottom ash (BA) has much better neutralization capacity than fly ash (FA), this compensating on a certain extent the fact that FA amount is three times larger than the BA one. The final mixture (F-m) has also good neutralization capacity (248 kg ash mixture for 1 m^3 of AMD). Another important finding is that the quality of neutralized water complies with the authorized limits, but the high amount of Mn in ash and neutralized water poses some regulatory issues.Based on these preliminary results it is considered that further researches are needed, mainly for the understanding of all the processes that take place in the system wood ash - AMD, and for the practical application.

References

1.*** QUANTIFICATION PROTOCOL: Energy generation from the combustion of biomass waste, Alberta Environment and Sustainable Resource Department, 2014.

2. PAVEL, P.B, PUSCHENREITER, M., WENZEL, W.W., DIACU, E., BARBU, C.H., Sci. Total Environ. 479-480, 2014, p.125.

3. ANDREI, B., DICU, M., POPESCU, N., ZELICI, L., Revista constructiilor, 11, 2014, p. 46.

4. MARMANDIU, M.A., POPESCU, R., PLOSCARIU, T., MOSNEAG, M., 2009, 1, p. 24.

5. KARER, J., WAWRA, A,, ZEHETNER, F., DUNST, G., WAGNER, M., PAVEL, P.B., PUSCHENREITER, M., FRIESL-HANL, W., SOJA, G.,. Water Air Soil Pollution, 2015, p. 226.

6. SARABER, A., HAASNOT, J., Proceedings of ASH 2012 Conference, Stockholm, Sweden, January 25-27, 2012.

7. PELS, J., Proceedings of ASH 2012 Conference, Stockholm, Sweden, January 25-27, 2012.

8. RESETAR-DEAC, A.-M., DIACU, E., Rev. Chim. (Bucharest), **66**, no.9, 2015, p.1535.

9. HERRICKS, E.H., Biological treatment of acid mine drainage, University Of Illinois, 1982.

10. KOOPMAN, B., Environmental uses: Acid Neutralization, in Kogel, J.E., Krukowski, S.T., Trivedi, N.C. Barker, J.M., (Editors), Industrial Minerals and Rocks: Commodities, Markets and Uses, Society for Mining, Metallurgy, and Exploration, 2006, p.1205.

11. BACKSTROM, M., SARTZ, L., 2013. Fly ash injection into weathered mine waste. In: BROWN, A., FIGUEROA, L., WOLKERSDORFER, C.H.: Reliable Mine Water Technology, I, 2013, p. 513.

12. HEVIÁNKOVA, S., SPAKOVSKA, B., KLIMKO, T., KYNCL, M., BILSKA, Z., KUÈEROVA, L., Carpathian Journal of Earth and Environmental Sciences, 9, no. 2, 2014, p.159.

13. VAN EIJK, R.J., OBERNBERGER, I., SUPANCIC, K., Bioenergy IEA - Options for increased utilization of ash from biomass combustion and co-firing, Report, Arnhem, 2012.

14.VADAPALLI, V.R.K., KLINK, M.J., ETCHEBERS, O., PETRIK, L.F., GITARI, W., WHITE, R.A., KEY D., IWUOHA E., S. Afr. J. Sci., 104, no.7-8, 2008, p. 317.

15.BARBU, C.H., PAVEL, P.B., MOISE, C.M., SAND, C., POP, M.R., IGNAT, E.G., Proceedings of the 11th International Conference on Environment, Ecosystems and Development (EED '13) - Pollution and Environmental Protection, World Scientific and Engineering Academy and Society (WSEAS) Conference, Brasov, 1-3 June 2013, p.187.

16. PAVEL, B.P., BARBU, C.H., SAND, C., POP, M.R., Metal Elements in Environment, Medicine and Biology, IX, 2009, p. 49.

17. VAN HERCK, P., VANDECASTEELE, C., Waste Manag., 21, 2001, p. 685.

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