Asian Journal of Chemistry; Vol. 24, No. 3 (2012), 1045-1050

ASIAN JOURNAL OF CHEMISTRY

www.asianjournalofchemistry.co.in

Fly Ash Zeolite as Permeable Reactive Barrier for Prevention of Groundwater Contamination Due to Coal Ash Disposal

BABLY PRASAD*, KUMARI SANGEETA and B.K. TEWARY

Central Institute of Mining and Fuel Research, Barwa Road, Dhanbad-826 015, India

*Corresponding author: E-mail: drbablyprasad@yahoo.com

(*Received*: 29 January 2011; *Accepted*: 3 November 2011) AJC-10590

Prevention of groundwater contamination by using permeable reactive barrier (PRB) or zeosynthetic liner is a new and innovative technology. Permeable reactive barrier's are constructed underground across the flow path of contaminated ground water. The contaminants are removed from contaminated water by geochemical process taking place in the reactive material of the permeable reactive barrier. The suitable materials used in permeable reactive barrier's are commonly activated carbon, zeolites, clay minerals and others. Fly ash produced due to burning of coal in thermal power plants can be converted into zeolitic mineral and the prepared zeolite can be used as permeable reactive barrier (zeosynthetic liner) to react with contaminants of leachate water of coal ash and make it clean. The process would reduce contamination of groundwater of coal ash filled pond or abandoned opencast mine, if the ash pond or open cast mine is filled with coal ash and lining of fly ash zeolite at its bottom. In the present work, laboratory scale study has been carried out to convert fly ash into fly ash zeolite and the prepared fly ash zeolite has been used as permeable reactive barrier and found that it can be successfully utilize as effective permeable reactive barrier (zeosynthetic liner) for prevention of groundwater contamination.

Key Words: Fly ash, Zeolite, Groundwater, Coal ash.

INTRODUCTION

Prevention of groundwater contamination by using permeable reactive barrier (PRB) or geosynthetic liner is a new and innovative technology[1]. In India more than 100 million tonnes of coal ash are generated due to burning of coal in thermal power plants. A few percentage of ash is utilized in different sectors like cement, concrete and bricks industry *etc*. Rest coal ash is disposed off to ash disposal pond/low lying area with high environmental risk[2]. Ground water contamination due to coal ash disposal is very much possible as the leachate water of coal ash may percolate through surface of pervious ground and reach groundwater[3,4]. One of the very useful utilization of fly ash is preparation of fly ash zeolite (FAZ) as value aided product[5]. This fly ash zeolite has much utilization for protection of the environment[6-10]. Utilization of fly ash zeolite as permeable reactive barrier or geosynthetic liner for remediation of groundwater contamination due to disposal of ash into ash pond or abandoned opencast mine is a cost effective as well as new technology[11]. The objective of the present work is to investigate the utilization of fly ash zeolite as geosynthetic liner/permeable reactive barrier for disposal of coal ash into abandoned opencast mine. The experiment has been carried out at laboratory scale.

EXPERIMENTAL

Concept of permeable reactive barrier/geosynthetic liner: Permeable reactive barriers for groundwater remediation, as first developed in North America. This is a significantly cost effective technique for remediation of shallow aquifers and therefore contributes to the prevention of groundwater resources[12]. Permeable reactive barriers (Fig. 1) are defined as passive *in situ* treatment zone of reactive material that degrades or immobilises contaminants as contaminated water flows through it[12]. The contaminants are removed from groundwater flow by geochemical process such as surface adsorption, chemical bonding, redox reaction, ion exchange and/or precipitation. The permeable reactive barrier technology appears to be a promising approach to effective groundwater remediation. Natural zeolite as well as fly ash zeolite prepared from coal fly ash can be applied as permeable reactive barrier technology because of the high sorption and ion exchange capacity of the materials[13].

Laboratory experiment: The fly ash obtained from burning of coal in power plants can be treated in alkaline hydrothermal condition using NaOH. The method can be made economically viable by recycling the NaOH solution, optimum temperature and minimum solid:liquid ratio of fly ash and alkali. In the present work fly ash zeolite was prepared from fly ash which was obtained from Talcher super thermal power plants of NTPC of Odisha State. The obtained raw fly ash sample was bench dried and used as such without screening. The unburnt carbon and volatile materials present in fly ash was removed by calcinations at 800 ºC for 1 h. Hydrothermal activation of fly ash has been carried out with NaOH treatment. The experiment used an open reflux method. According to earlier work[14] the fly ash conversion was carried out to obtain cost effective zeolite synthesis (NaOH as activation agent, temperature 100 ± 5 ºC, conversion time 24 h, solution concentration of 2 M, solution/sample ratio of 5:1). The transformed fly ash was filtered and washed repeatedly with deionized water until the pH of the wash water reached 8-9. The product was dried in an oven at 45-50 ºC and kept in powder form until further use.

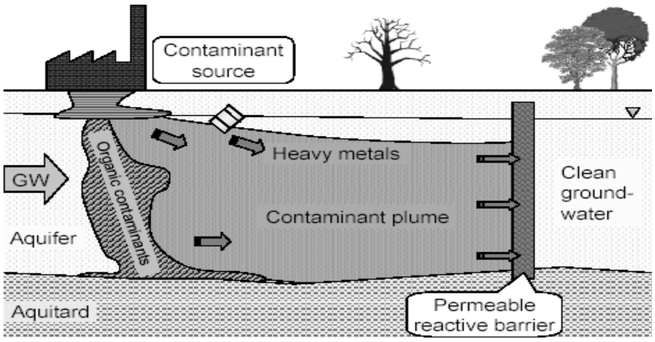

Fig. 1. Schematic diagram showing permeable reactive barrier concept (Roehl, 2004).

Characterization of fly ash zeolite: The phase characterization of fly ash and prepared fly ash zeolite was carried out by X-ray diffraction (XRD) using a D-8 Advance Bruker AXS model, Germany. The morphology of fly ash and prepared zeolites were recorded on Camscan series 4 scanning electron microscope.

Leaching experiment: To study the capacity of fly ash zeolite if used as geosynthetic liner for ash disposal into ash pond/abandoned opencast mine, laboratory experiment was carried out. In this experiment two box type vats were prepared (Fig. 2). Vats used for leaching experiment had 28.8 cm length and 28.6 cm breath. Both vats were open at one end and closed at the other end with a small hole to be used for the collection of leachate water. The collected leachate water was supposed to enter ground water in field condition. Talcher pond ash was used for the leaching experiment. 15 kg of Talcher pond ash was taken in a vat, which contained no liner and the other vat contained liner of 2 kg Talcher fly ash zeolite as a bed at the bottom and 13 kg of Talcher pond ash above it. Pore volume of pond ash kept in vats was determined by using ASTM standard (D 4874-95).

Every week half pore volume of deionized water was passed through each vat filled with pond ash. Two pore volume of water passed through the vats every month. The experiment was continued for nearly 21 months. After passing each half pore volume of water through the vats, leachate water was collected from the bottom of the vats and analysis of different parameters were carried out. The parameters analyzed were pH, total hardness, calcium hardness, magnesium hardness, chloride, sulphate, total dissolved solid and heavy metals. After completion of the vat leaching experiment, the obtained data were processed to know the effect of fly ash zeolite if used as geosynthetic liner (reactive permeable barrier) for disposal of ash into ash pond/abandoned opencast mine.

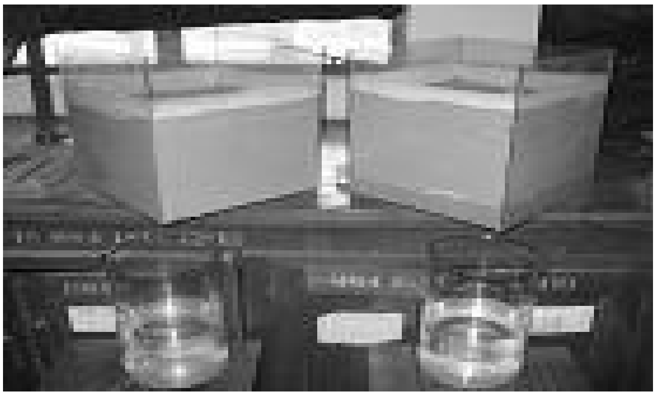

Fig. 2. Laboratory leaching experiment showing one vat with only pond ash and other vat containing pond ash with liner

RESULTS AND DISCUSSION

Characterization: XRD analysis was conducted on the raw fly ash and fly ash zeolite in order to determine the crystalline phases present in the initial material before and after zeolite synthesis (Fig. 3a and 3b). Fig. 3a shows that the predominant crystalline phases present in the fly ash were quartz (SiO_2) and mullite ($Al_6Si_2O_{13}$). Fig. 3b indicates that more crystalline fly ash zeolite phase has been formed during the experiment. Different types of zeolites have been prepared by reacting fly ash with different concentrations of NaOH solution at 100 ± 5 ºC for 24 h. Different zeolites showed characteristic peak on diffractogram. It has been observed that the main zeolite formed is zeolite NaP1 followed by fauzasite and chabazite. Fig. 4a and 4b shows the SEM photomicrographs of fly ash particles before and after alkaline treatment. The fly ash particles (Fig. 4a) before treatment are spherical in nature and have a smooth surface due to a covering of alumino-silicate glass. The absence of spherical particles and development of rough surfaces in treated fly ash (Fig. 4b) indicates that zeolite was formed on the surface of fly ash particles due to alkaline hydrothermal treatment.

Leaching experiment: Laboratory vat leaching experiment carried out with one vat filled only with 15 kg of Talcher pond ash and other vat filled with 2 kg of fly ash zeolite (which covered the bottom of the vat) and above it 13 kg of Talcher pond ash. In the second vat fly ash zeolite worked as zeosynthetic liner (permeable reactive barrier) through, which leachates of pond ash percolated down. Leachates were collected after every half pore volume of water passed through both the pond ash filled vats. Analysis of different water quality parameters were carried out.

The initial pH of leachate water collected from the vat with liner after passing half pore volume of water was 8.5 and the pH value of leachate water initially collected after passing half pore volume of water through vat without liner was 8.16 (Fig. 5).

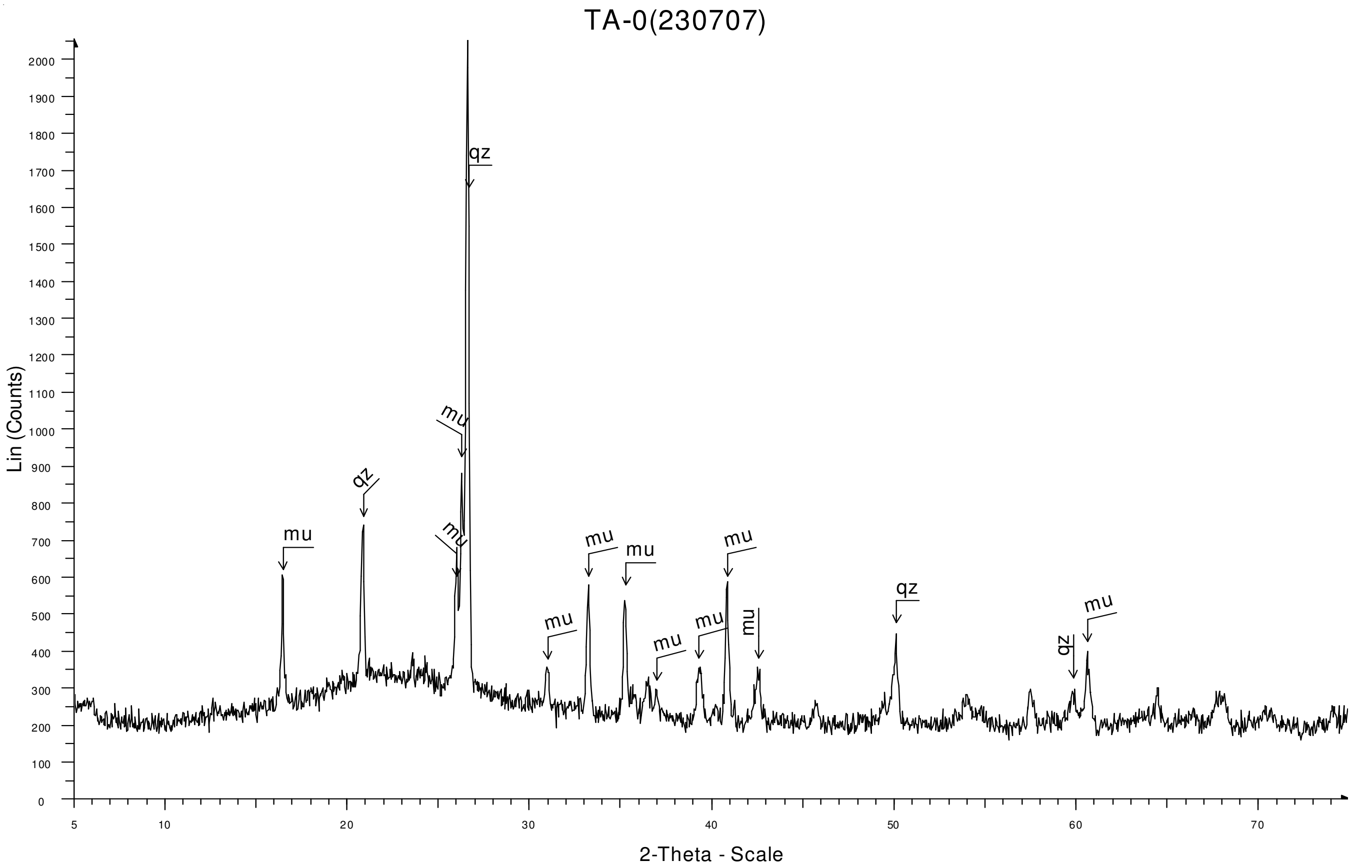

Fig. 3a. XRD pattern of Talcher fly ash

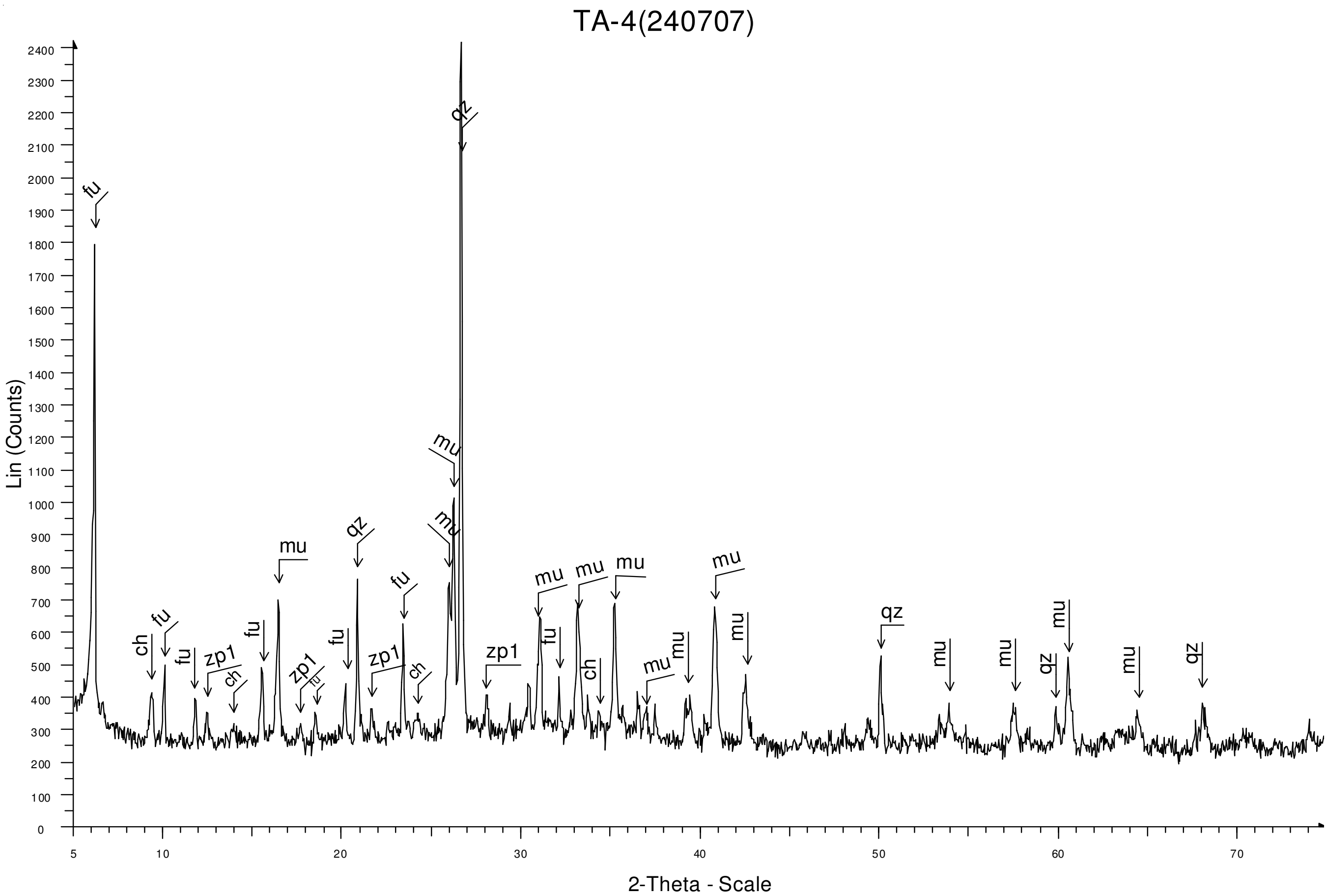

Fig. 3b. XRD pattern of Talcher fly ash zeolite

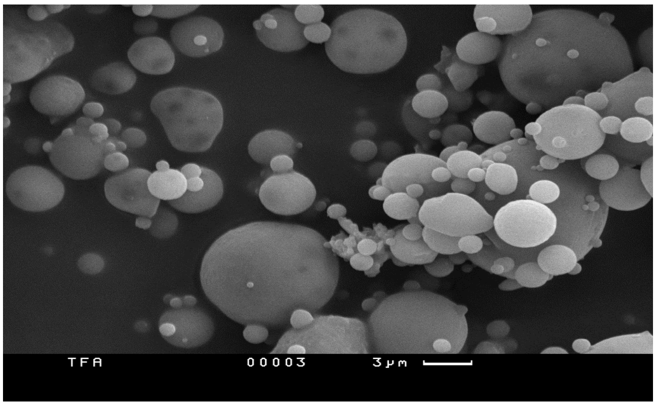

Fig. 4a. SEM Photograph of Talcher flyash

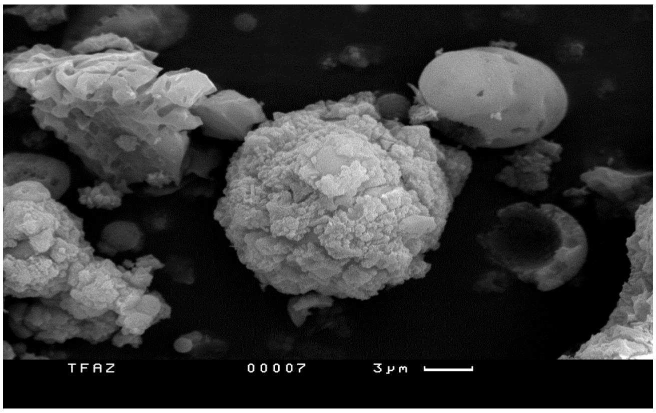

Fig. 4b. SEM Photograph of Talcher flyash zeolite

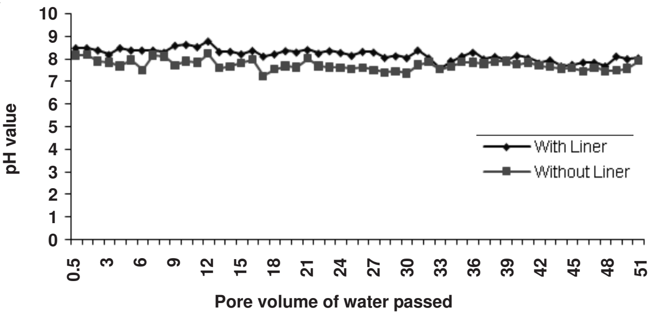

Fig. 5. pH value of collected leachate

A little increased pH value in leachate of pond ash filled vat with liner was due to alkaline nature of fly ash zeolite which was used as liner in the vat. Gradual decrease in pH value of leachate water was observed as more and more pore volume of water was passed through the vats.

The initial total hardness of leachate water collected from the vat with liner was only 8 mg/L whereas total hardness of initial leachate water collected after passing half pore volume of water through the vat without liner was 304 mg/L (Fig. 6). It was observed that the fly ash zeolite liner was effective in removing total hardness from leachate water of pond ash. Throughout the experiment it was observed that total hardness of leachate water was completely removed by the zeolitic liner which was used in one pond ash filled vat.

Calcium hardness in leachate water, collected after passing half pore volume of water through pond ash filled vat with liner, was found nil. Whereas in similar condition leachate water of pond ash filled vat without liner showed 160 mg/L of calcium hardness (Fig. 7). Throughout the experiment, up to 51 pore volume of water (306 L) which was passed through the ash filled vat with liner, no calcium hardness was detected in leachate water collected from the bottom of the vat.

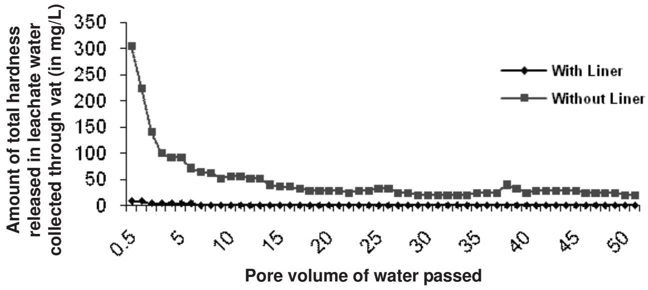

Fig. 6. Concentration of total hardness of collected leachates

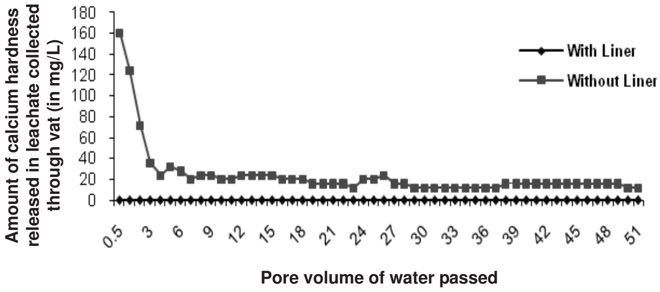

Fig. 7. Concentration of calcium hardness of collected leachates

Concentration of magnesium hardness in leachate water was evaluated by calculation using total hardness and calcium hardness data. In the beginning magnesium hardness in leachate water of vat with liner was 1.944 mg/L whereas it was 34.99 mg/L in leachate water of vat without liner (Fig. 8). After passing 7 pore volume of water, magnesium hardness in leachate water of vat with liner became nil, whereas gradual decease in its concentration was observed in leachate water of vat without liner.

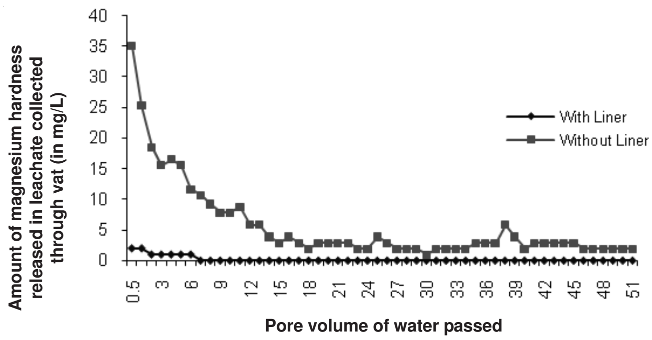

Fig. 8. Concentration of magnesium hardness of collected leachates

Chloride content in leachate water collected after passing half pore volume of water present through pond ash filled vat with liner was 32 mg/L and pond ash filled vat without liner was 84 mg/L. It indicated that fly ash zeolite liner is also helpful in reducing the concentration of chloride in leachate water in the beginning itself (Fig. 9). The reduction in chloride content was due to its precipitation/adsorption in fly ash zeolite liner phase.

After passing half pore volume of water through pond ash filled vat with liner, the concentration of sulphate in collected leachate water was 28.84 mg/L, whereas in similar condition its concentration was 43.26 mg/L in leachate water of pond ash filled vat without liner (Fig. 10). Due to lining of fly ash zeolite a reduction in the concentration of sulphate in leachate water was observed. This may be due to precipitation of sulphate in fly ash zeolite liner phase. Decreasing as well as irregular trend in sulphate concentration was observed in collected leachate water of both the vats at different pore volumes.

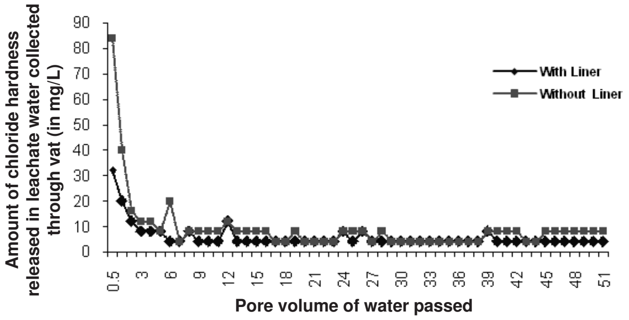

Fig. 9. Concentration of chloride in collected leachates

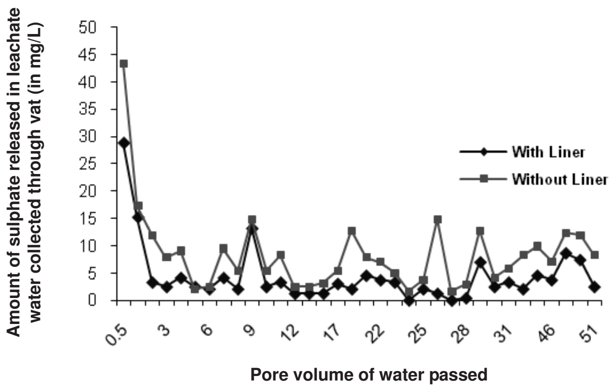

Fig. 10. Concentration of sulphate in collected leachates

The concentration of total dissolved solids in leachate water collected after passing half pore volume of water through pond ash filled vat with liner was 543 mg/L, whereas it was 491 mg/L in leachate water of vat without liner (Fig. 11). An opposite trend was observed in case of total dissolved solid. Due to presence of liner there was an increase in total dissolved solid value in leachate water in comparison to leachate water which was collected from vat without liner. This was due to dissolution of unreacted sodium hydroxide into leachate water which was initially present in fly ash zeolite liner.

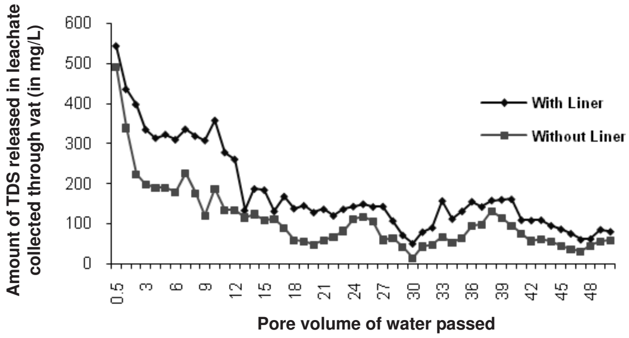

Fig. 11. Total amount of TDS present in collected leachates

Heavy metals analysis in the collected leachate water through pond ash filled vat without liner, after every 5 pore volume of water passed through it, revealed that lower concentrations of heavy metals were released in leachate water. The concentrations of all metals were varying in each analysis (Tables-1-3). The release of heavy metals like Cu, Mn, Zn, Pb, Ni, Cd and Cr were less than 0.10 mg/L in each leachate that was collected after passing 5 pore volume of water through vat. The maximum concentrations of heavy metals that were released in the leachates were 1.091 mg/L Fe, 0.104 mg/L Pb, 0.059 mg/L Zn, 0.055 mg/L Cu, 0.028 mg/L Mn, 0.0219 mg/L Ni, 0.00062 mg/L Cd and 0.01389mg/L Cr.

TABLE-1
CONCENTRATION OF HEAVY METALS IN COLLECTED LEACHATES (mg/L)

Pore vol.	Iron (Fe)		Lead (Pb)		Zinc (Zn)	
	With liner	Without liner	With liner	Without liner	With liner	Without liner
0.5	0.092	0.895	0.070	0.093	**0.022**	**0.059**
1.5	0.049	**1.091**	0.066	**0.104**	0.017	0.042
5.0	**0.487**	0.829	0.065	0.088	0.021	0.035
10	0.285	0.585	0.066	0.086	0.007	0.041
15	0.196	0.539	0.073	0.101	0.015	0.044
20	0.238	0.450	0.072	0.102	0.014	0.039
25	0.222	0.334	**0.081**	0.095	0.008	0.035
30	0.135	0.119	0.036	0.051	0.017	0.038
35	0.070	0.141	0.041	0.048	0.019	0.020
40	0.202	0.254	0.081	0.095	0.020	0.042
45	0.105	0.278	0.066	0.082	0.015	0.030
50	0.196	0.209	0.081	0.094	0.014	0.042

TABLE-2
CONCENTRATION OF HEAVY METALS IN COLLECTED LEACHATES (mg/L)

Pore vol.	Copper (Cu)		Manganese (Mn)	
	With liner	Without liner	With liner	Without liner
0.5	0.003	0.008	0.005	0.015
1.5	0.002	0.007	0.006	0.015
5.0	0.003	0.005	**0.008**	**0.028**
10	**0.007**	0.011	**0.008**	0.014
15	0.001	**0.055**	0.006	0.013
20	0.000	0.016	0.004	0.015
25	0.000	0.005	0.004	0.006
30	0.000	0.002	0.002	0.003
35	0.000	0.005	0.001	0.009
40	0.000	0.006	0.005	0.007
45	0.000	0.006	0.004	0.008
50	0.000	0.004	0.003	0.005

Heavy metals analysis in collected leachate water through pond ash filled vat with liner after every 5 pore volume of water passed through it revealed that due to presence of fly ash zeolite liner the concentrations of heavy metals are lesser than in leachate of pond ash filled vat without liner. It indicates that fly ash zeolite liner is quite effective in reducing the concentrations of heavy metals in leachate water. Maximum leaching of heavy metals like Fe, Pb, Zn, Cu, Mn, Ni, Cd and Cr observed at different pore volume of water passed through the vat with liner and the concentrations were 0.487 mg/L Fe, 0.081 mg/L Pb, 0.022 mg/L Zn, 0.007 mg/L Cu, 0.008 mg/L Mn, 0.0061 mg/L Ni, 0.00025 mg/L Cd and 0.0135 mg/L Cr. Comparing the amount of maximum release of heavy metals in leachate water collected from both the vat shows that release of heavy metals are quite lesser in leachate of pond ash filled vat with liner as compared to pond ash filled vat without liner.

TABLE-3
CONCENTRATION OF HEAVY METALS IN LEACHATE WATER (mg/L)

Pore vol.	Nickel (Ni)		Cadmium (Cd)		Chromium (Cr)	
	With liner	Without liner	With liner	Without liner	With liner	Without liner
0.5	**0.0061**	**0.0219**	0.00013	0.00037	**0.0135**	**0.01389**
1.5	0.0044	0.0065	0.00016	0.00026	0.0063	0.0117
5.0	0.0036	0.0035	0.00016	0.00025	0.0020	0.0028
10	0.0025	0.0066	0.00013	0.00026	0.0041	0.0111
15	0.0015	0.0030	0.00019	0.00026	0.0005	0.0055
20	0.0013	0.0066	0.00023	0.00046	0.0004	0.0061
25	0.0019	0.0026	0.00018	0.00027	0.00042	0.0066
30	0.0015	0.0023	0.00015	0.00027	0.00020	0.0050
35	0.0014	0.0040	**0.00025**	**0.00062**	0.00022	0.0050
40	0.0014	0.0026	0.00018	0.00025	BDL	BDL
45	0.0013	0.0024	0.00016	0.00032	BDL	BDL
50	0.0016	0.0020	0.00019	0.00028	BDL	BDL

Conclusion

From the experiment it was observed that fly ash zeolite liner is very much effective in completely removing total hardness, Ca hardness and Mg hardness from leachate of pond ash filled vat with liner. The geosynthetic fly ash zeolite liner is also effective in significantly reducing the concentration of chloride and sulphate in leachate water of pond ash filled vat with liner as compared to leachate water of pond ash filled vat without liner. The leachate water of pond ash filled vat with liner showed a little higher pH and TDS as compared to leachate water of pond ash filled vat without liner. This is due to unreacted alkali present in fly ash zeolite, which leached out in leachate water responsible for higher pH and TDS. Fly ash zeolite liner has been found very effective in reducing the concentrations of heavy metals like Fe, Zn, Cu, Mn, Pb, Ni, Cd and Cr in leachate water of pond ash filled vat. As such low and irregular concentration of heavy metals released in leachate water of pond ash throughout the study period. The leachate water of pond ash filled vat with liner even contained very low concentration of heavy metals due to presence of liner. In laboratory scale fly ash zeolite liner has successfully experimented to know the effective utilization of it as geosynthetic liner. A field investigation is needed to be carried out for confirmation of utilization of fly ash zeolite liner for disposal of fly ash into abandoned opencast mine.

ACKNOWLEDGEMENTS

Authors are grateful to Ministry of Coal, Government of India for funding the grant-in-aid project for carrying out the investigation. Thanks are due to Dr. Amalendu Sinha, Director of Central Institute of Mining and Fuel Research, Dhanbad, India for the support during the investigation period. Thanks are also due to Dr. Sudip Maity, Scientist, CIMFR for carrying out XRD analysis.

REFERENCES

1. K.E. Roehl, P. Huttenloch, K. Czurda, in ed.: R.W. Sarsby and T. Meggyes, Permeable Sorption Barriers for *in-situ* Remediation of Polluted Groundwater Reactive Materials and Reaction Mechnism, Proc. Green3-, The Exploitation of Natural Resources and the Consequences, June 2000, Berlin, Thomas Telford Publ., London, pp. 466-473 (2001).
2. B. Prasad and K.K. Mondal, *Poll. Res.*, **26**, 55 (2007).
3. B. Prasad and K.K. Mondal, *Mine Water Environ.*, **27**, 40 (2008).
4. B. Prasad and K.K. Mondal, *Asian J. Water, Environ. Pollut.*, **4**, 17 (2007).
5. S. Rayalu, S.U. Meshram and M.Z. Hasan, *J. Hazard. Mater.*, **B77**, 123 (2000).
6. V. Somerset, L. Petrik and M. Klink, *Fresenius Environ. Bull.*, **14**, 1 (2005).
7. S. Wang, L. Li and Z.H. Zhu, *J. Hazard. Mater.*, **B139**, 254 (2007).
8. J. Chen, H. Kong, D. Wu, Z. Hu, Z. Wang and Y. Wang, *J. Colloid. Interf. Sci.*, **300**, 491 (2006).
9. V. Somerset, L. Petrik and E. Iwuoha, *J. Environ. Manage.*, **87**, 125 (2008).
10. E. Otal, F. Vilches Luis, N. Moreno and X. Querol, *Fuel,* **84**, 1440 (2005).
11. B. Prasad, Investigation into Low Cost Liner for Disposal of Coal Ash in Abandoned Opencast Mines. Project No. EE/34, Ministry of Coal, Government of India, February 2010.
12. K.E. Rochl, Passive *in situ* Remediation of Contaminated Groundwater: Permeable Reactive Barriers- PRBs. Groundwater Management in Mining Areas. CP-035, Germany, pp. 57-70 (2004).
13. K.A. Czurda and R. Haus, *Appl. Clay Sci.*, **21**, 13 (2002).
14. B. Prasad, S. Kumari, A.K. Mahato, S. Maity and R. Mortimer, *Environ. Technol.*, (In Press).