Oil Shale, 2010, Vol. 27, No. 3, pp. 250–257
doi: 10.3176/oil.2010.3.06 ISSN 0208-189X

EFFECT OF OIL SHALE ASH APPLICATION ON LEACHING BEHAVIOR OF ARABLE SOILS: AN EXPERIMENTAL STUDY

J. ADAMSON[(a)], N. IRHA[(a)*], K. ADAMSON[(a)], E. STEINNES[(b)], U. KIRSO[(a)]

[(a)] National Institute of Chemical Physics and Biophysics, Akadeemia tee 23, 12618 Tallinn, Estonia;
[(b)] Norwegian University of Science and Technology, Department of Chemistry, N-7491 Trondheim, Norway

Oil shale ash contains mineral ingredients of agricultural importance and could be used for treatment of soils. However, the ash contains several hazardous ingredients, i.e. toxic trace metals which could be mobile and create environmental concerns. Beneficial use of the oil shale ash in agriculture and forestry requires better knowledge of leaching characteristics of soil-ash systems. In this study two different ash samples have been added to two types of soil, particularly Rendzic Leptosol *and* Podzolic Gleysols, *in order to investigate the leaching characteristics of soil/ash mixtures using the traditional leaching scheme and a scheme modified by pretreatment (incubation) of solid in wet conditions. The pH, conductivity and concentration of Cd, Pb, Cr, Zn and Ni in leachates are determined. The results revealed that transport of hazard components to the water phase was highly dependent on the type of soil and ash and leaching method used. Throughout the experiment, concentrations of heavy metals in leachates of any combination of soil and fly ash are low. The most mobile metals are found to be nickel, zinc and chromium. Application of oil shale ash to soil might increase mobile fraction of Ni in soil.*

For the safe recycling of oil shale wastes in agriculture, it is recommended to take into account the leaching behavior of trace elements as ingredients in combustion ash.

Introduction

Large quantities of solid wastes from fossil fuels generated each year and increasing costs of landfilling support development of methods for beneficial recycling of combustion ash [1, 2]. As an alternative to landfilling, some of

* Corresponding author: e-mail *natalja.irha@kbfi.ee*

the ash fractions have been used for soil amendment [3–7]. Particularly in Estonia energy production has been based on the combustion of oil shale resulting in a huge amount of ash. The massive ash materials have been a potential resource for agricultural applications. The most common mineral ingredients of agricultural importance in oil shale ash are: CaO (30–44%) as a liming agent, SiO_2 (27–32%), K_2O (2.7–7.0%) as a fertilizer, and Fe_2O_3 (5.2–5.5%) [8]. However, oil shale ash contains also trace elements [9, 10], which can be leached into soil, surface water and groundwater [2, 11–17]. Leachability of these elements is closely related to the phases to which they are associated as well as to pH of the leaching environment [2, 11]. Under wet conditions hydration, carbonation and subsequent transformation of oil shale waste resulted in different secondary Ca minerals [8, 17, 18]. A recent study by Riehl and coworkers found that the soil properties and mobilization potential of trace elements might change due to ash-soil-water interaction [19]. Taking into account the development of new technologies for oil shale processing and the high amount of generated ash it is recommended to increase the use of oil shale ash in several areas, including agriculture. Before the large-scale use, estimation of the risk derived from the application of ash is needed, which in turn requires better knowledge about leaching properties of soil/ash mixtures.

The aim of the present study is to investigate the effect of oil shale ash application on leaching properties of soil. Two approaches are chosen for leaching experiments: 1) a traditional one step leaching scheme and 2) pretreatment, i.e. incubation of the material in wet conditions imitating the field conditions, followed by a traditional leaching procedure keeping the total amount of water constant.

Materials and methods

Experimental part

Samples of two agricultural soils, i.e. *Rendzic Leptosol* (soil A) and *Podsolic Gleysols* (soil B) with content of organic matter (OM) 22.94% and 18.64% respectively, and different content of carbonates and clay minerals [20] were treated with deionized water separately and in a mixture with oil shale ash. The ash samples used in the experiments were taken from the exit gas flow duct of the first unit of electric precipitators of a boiler working on circulated fluidized-bed technology (CFB) and from the cyclone of a boiler based on pulverized firing combustion (PF) of oil shale (power plant AS Narva Elektrijaamad, Estonia). The main composition of the ash samples is characterized by different contents of quartz, calcite and lime [18, 21].

All soil samples were air-dried, crushed, and sieved through a 2-mm mesh. Samples of soils were mixed with ash (5:1 w/w) [22] for preparing dry mixtures.

The following traditional leaching procedure was applied. Each 60 g soil or soil/ash mixture sample was extracted with deionised water (liquid/solid ratio of 2.5 l/kg) for 24 hours. At the end of the extraction period, the solute was removed through a 0.45 µm filter (HIMFIL, Tallinn, Estonia).

For the modified leaching procedure with pretreated solid, 60 g of soil or soil/ash mixture sample was incubated with a small amount of deionized water (30 ml) for 7 days at room temperature. Then 120 ml of deionized water was added to keep the total amount of water constant. Pretreated sample was extracted for 24 hours. The liquid and the solid phase were separated by filtration through a 0.45 µm filter.

The water extracts (leachates) were used for further chemical analysis. All experiments were performed twice.

Chemical analysis

The following parameters of the leachates were determined: pH, electrical conductivity (EC), and the concentrations of potentially hazardous metals Cd, Cr, Ni, Pb and Zn. The pH and EC of the leachates were measured using a BENCH PC 510 pH/Conductivity Meter (Eutech Instruments Pte Ltd, Singapore/Oakland Instruments, Vernon Hills, IL, USA). The electrode was calibrated with pH buffer solutions before pH determination. Leachate samples were analyzed for Cd, Pb, Cr, Zn and Ni by graphite furnace AAS [23, 24]. Blank tests without sample but applying the same procedure were carried out in parallel for each set of analyses.

Results and discussion

The pH, electric conductivity (EC) values and concentration of selected heavy metals in leachates are listed in Table 1. The water extracts of all soil/ash mixtures are very alkaline. The pH values are slightly lower in leachates from incubated soil/PF ash mixtures and soil A/CFB ash mixture than in samples from the traditional leaching scheme. The concentration of dissolved mineral salts (EC) varies significantly for samples of soil/CFB ash mixtures as compared with soil/PF ash mixtures (Table 1).

The affinity of metals to solid is found to be different depending on metal and leaching conditions. Regardless of the method the concentrations of leached Cd and Pb are very low and need not to be taken into consideration (Table 1). Concentrations of metals in leachates from soil/ash mixtures decreases as follows: Ni > Zn > Cr (Table 1). Concentration range of Zn is similar to the leachate of alkaline lignite fly ash [15]. Incubation of soil/ash mixtures in wet conditions affect mobile fraction of metals (Fig. 1). Concentrations of both Ni and Zn in leachates from incubated soil/PF ash mixtures are 1.3–2.9 times higher than their concentrations in traditional samples. At the same time the concentrations of mobile Ni and Zn in incubated soil mixtures with CFB ash are less than those in traditional samples. In contrast, leaching behavior of Cr is characterized by lower amount of mobile metal in incubated soil/PF ash mixtures and soil A mixed with CFB ash as compared to traditional samples.

Table 1. **Leaching of total (evaluated by electric conductivity, EC, mS cm^{-1}) and alkaline (pH value) matrix components, and selected trace metals (concentration, μg l^{-1}) from soils and soil/ash mixtures**

Para-meters	Soil A	Soil B	Soil A/PF ash	Soil A/CFB ash	Soil B/PF ash	Soil B/CFB ash
Traditional leaching procedure						
pH	7.25	7.89	12.71	11.95	12.74	12.29
EC	0.865	0.84	9.02	2.94	9.72	5.94
Cd	<0.1	0.1	<0.1	<0.1	0.1	<0.1
Pb	2	<1	<1	<1	<1	<1
Cr	5	5	3	10	4	13
Zn	50	52	30	20	30	35
Ni	10	12	70	220	160	150
Leaching procedure with incubating						
pH	8.11	7.86	12.55	11.75	12.51	12.71
EC	0.528	1.16	8.20	7.24	9.65	9.06
Cd	<0.1	<0.1	<0.1	<0.1	0.1	<0.1
Pb	<1	<1	1	<1	1	<1
Cr	3	3	2	5	3	40
Zn	28	20	40	8	44	13
Ni	17	24	200	60	260	54

SD: pH ± 1%, EC ± 5%, metals ± 10%

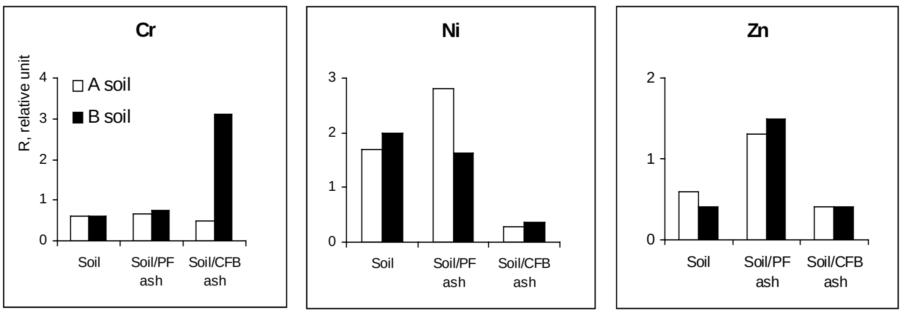

Fig. 1. Role of leaching method on mobile fraction of chromium, nickel and zinc in native soils and their mixtures with ash.
R, relative unit is the ratio of metal content (μg l^{-1}) in leachates from incubated soils or soil/ash mixtures to metal content (μg l^{-1}) in leachates of soils or soil/ash mixtures from traditional (i.e. without incubation) leaching procedure.
Soil A – *Rendzic Leptosol*; soil B – *Podzolic Gleysol.*
Combustion ash: PF – pulverized firing technology; CFB – circulated fluidized bed technology.

Leaching data reveals that adding CFB ash to soil B could result in an increased concentration of mobile Cr in soil (Table 1). In this case the penetration of Cr into groundwater is possible due to low affinity of soil towards Cr [24]. Thus, among the studied metals nickel, zinc and chromium are the most mobile metals.

Available data [10, 20, 25] revealed similar content of Cr, Zn and Ni in soils and in PF cyclone ash (Table 2). When the proportions of mobile metal in leachates from soils and soil/ash mixtures are compared, it is observed that among elements Ni is the metal for which the highest proportions in water extracts of treated soil/PF ash mixtures compared to pure soil samples are found (Table 3). Obtained data for Ni mobility is in good agreement with finding of Riehl et al. [19], which indicated a higher mobility of metal in rich calcium carbonate incubated soil amended with alkaline coal fly ash.

It is known that at elevated concentrations or availability the Cr, Ni and Zn may be toxic and they are active migrants in biogeochemical food webs [2, 11]. In this context it is important to note that concentrations of metals are well below the regulation standards.

Table 2. **Content of Cr, Zn and Ni (ppm) in soils [19, 27] and PF cyclone ash [10]**

Element	Soil A	Soil B	PF cyclone ash
Cr	48–62	37–48	20.8
Zn	80.1	79.9	93.0
Ni	23–30	18–23	25.4

Table 3. **Proportions of mobile Cr, Zn and Ni (% on total content) in leachates from soils and soil/PF ash mixtures**

Object	Traditional leaching procedure	Leaching procedure with incubating
	Cr	
Soil A	0.02–0.03	0.01–0.02
Soil B	0.03	0.02
Soil A/PF ash	0.01–0.02	0.01
Soil B/PF ash	0.02–0.03	0.02
	Zn	
Soil A	0.16	0.05
Soil B	0.16	0.06
Soil A/PF ash	0.09	0.12
Soil B/PF ash	0.09	0.13
	Ni	
Soil A	0.08–0.11	0.14–0.18
Soil B	0.13–0.17	0.26–0.33
Soil A/PF ash	0.60–0.75	1.71–2.14
Soil B/PF ash	1.74–2.22	2.78–3.38

Depending on the properties of ash and soil, time of interaction in wet conditions the pH of mixture may vary, ultimately affecting the leachability of trace elements.

In general, two kinds of effects should be considered when applying the waste in agriculture: short-term effects due to readily bioavailable forms of metals from the waste, and long-term effects resulting from the dynamics in metal speciation or other biogeochemical processes in the soil-plant system following waste application [2, 26, 27].

Conclusions

Soil/ash mixtures are treated with water in order to evaluate leaching characteristics and mobilization potential of list of metals during soil-ash-water interaction.

The transport of soil/ash mixture components to the water phase is highly dependent on the type of soil, ash and leaching conditions.

Heavy metal concentrations in the leachates are well below the regulation standards.

Application of oil shale ash to soil might increase concentration of soluble salts and mobile fraction of Ni in soil.

For safe recycling of oil shale wastes in agriculture, it is advisable to take into account the leaching of trace elements from combustion ash-amended soils.

Acknowledgements

This study was supported by Estonian Research Council Targeted Financing Project SF0690001s09 and Estonian Science Foundation, Grant No 6828. The authors express their thanks to Dr. V. Petersell for providing soil samples and MSc K. Joa for kind help, and also thanks to Ms. P. Laas for technical assistance.

REFERENCES

1. *Jala, S., Goyal, D.* Fly ash as a soil ameliorant for improving crop production - a review // Bioresource Technol. 2006. Vol. 97, No. 9. P. 1136–1147.
2. *Jankowski, J., Ward, C. R., French, D., Groves, S.* Mobility of trace elements from selected Australian fly ashes and its potential impact on aquatic ecosystems // Fuel. 2006. Vol. 85, No. 2. P. 243–256.
3. *Kikas, V. H.* Mineral matter of kukersite oil shale and its utilization // Oil Shale. 1988. Vol. 5, No. 1. P. 15–27 [in Russian].
4. *Turbas, E.* Use of oil-shale ashes as a lime fertilizer in Estonia // Oil Shale. 1992. Vol. 9, No. 4. P. 301–309 [in Russian].

5. *Gangloff, W. J., Ghodrati, M., Sims, J. T., Vasilas, B. L.* Field study: influence of fly ash on leachate composition in an excessively drained soil // J. Environ. Qual. 1997. Vol. 26. P. 714–723.
6. *Clark, R. B., Ritchey, K. D., Baligar, V. C.* Benefits and constraints for use of FGD products on agricultural land // Fuel. 2001. Vol. 80, No. 6. P. 821–828.
7. *Sajawan, K. S., Paramasivam, S., Alva, A. K., Adriano, D. C., Hooda, P. S.* Assessing the feasibility of land application of fly ash, sewage sludge and their mixtures // Adv. Environ. Res. 2003. Vol. 8, No. 1. P. 77–91.
8. *Saether, O. M., Banks, D., Kirso, U., Bityukova, L., Sorlie, J.-E.* The chemistry and mineralogy of waste from retorting and combustion of oil shale // In: Energy, Waste, and the Environment: a Geochemical Perspective / R. Giere, P. Stille (eds.). London: Geological Society, Special Publication, 2004. P. 263–284.
9. *Pets, L., Vaganov, P., Knoth, J., Haldna, Ü., Shwenke, H.,Schnier, C., Juga, R.* Microelements in oil-shale ash of the Baltic Thermoelectric Power Plant // Oil Shale. 1985. Vol. 2, No. 4. P. 379–390 [in Russian].
10. *Häsänen, E., Aunela-Tapola, L., Kinnunen, V., Larjava, K., Mehtonen, A., Salmikangas, T., Leskelä, J., Loosaar, J.* Emission factors and annual emissions of bulk and trace elements from oil shale fueled power plants // Sci. Total Environ. 1997. Vol. 198, No. 1. P. 1–12.
11. *Adriano D. C.* Trace Elements in Terrestrial Environments. 2nd ed. – New York: Springer-Verlag, 2001.
12. *Wright, R. J., Codling, E. E., Stuczynski, T., Siddaramappa, R.* Influence of soil-applied coal combustion by-products on growth and elemental composition of annual ryegrass // Environ. Geochem. Hlth. 1998. Vol. 20, No. 1. P. 11–18.
13. *Tripathi, R. D., Vajpayee, P., Singh, N., Rai, U. N., Kumar, A., Ali, M. B., Kumar, B. Yunus, M.* Efficacy of various amendments for amelioration of fly-ash toxicity: growth performance and metal composition of Cassia siamea Lamk // Chemosphere. 2004. Vol. 54, No. 11. P. 1581–1588.
14. *Kirso, U., Irha, N., Reinik, J., Urb, G., Laja, M.* The role of laboratory and field leaching tests in hazard identification for solid materials // ATLA. 2007. Vol. 35, No. 1. P. 119–122.
15. *Ram, L., Srivastava, N. K., Tripathi, R. S., Thakur, S. K., Sinha, A. K., Jha, S. K., Masto, R. E., Mitra, S.* Leaching behavior of lignite fly ash with shake and column tests // Environ. Geol. 2007. Vol. 51, No. 7. P. 1119–1132.
16. *Raave, H., Kapak, S., Orupõld, K.* Phytotoxicity of oil shale semi-coke and its aqueous extracts: a study by seed germination bioassay // Oil Shale. 2007. Vol. 24, No 1. P. 59–72.
17. *Dellantonio, A., Fitz, W. J., Custovic, H., Repmann, F., Schneider, B. U., Grünewald, H., Gruber, V., Zgorelec, Z., Zerem, N., Carter, C., Marcovic, M., Puschenreiter, M., Wenzel, W. W.* Environmental risks of farmed and barren alkaline coal ash landfills in Tuzla, Bosnia and Herzegovina // Environ. Pollut. 2008. Vol. 153, No. 3. P. 677–686.
18. *Uibu, M., Uus, M., Kuusik, R.* CO_2 mineral sequestration in oil-shale wastes from Estonian power production // Environ. Manage. 2009. Vol. 90, No. 2. P. 1253–1260.
19. *Riehl, A., Elsass, F., Duplay, J., Huber, F., Trautmann, M.* Changes in soil properties in a fluvisol (calcaric) amended with coal fly ash // Geoderma. 2010. Vol. 155, No. 1–2. P. 67–74.

20. *Petersell, V., Mõttus, V., Täht, K., Unt, L.* Bulletin of the Geochemical Monitoring of Soil 1992 – 1994. – Geological Survey of Estonia, Department of Environmental Geology. Tallinn, 1996.
21. *Kuusik, R, Uibu, M, Kirsimäe, K.* Characterization of oil shale ashes formed at industrial-scale CFBC boilers // Oil Shale. 2005. Vol. 22, No. 4S. P. 407–420.
22. *Pathan, S. M., Aylmore, L. A. G., Colmer, T. D.* Properties of several fly ash materials in relation to use as soil amendments // J. Environ. Qual. 2003. Vol. 32, No. 2. P. 687–693.
23. Trace Elements in Natural Waters / B. Salbu, E. Steinnes (eds.). – Boca Raton, FL: CRC Press, 1995.
24. *Irha, N., Steinnes, E., Kirso, U., Petersell, V.* Mobility of Cd, Pb, Cu, and Cr in some Estonian soil types // Est. J. Earth Sci. 2009. Vol. 58, No. 3. P. 209–214.
25. *Peteresell, V., Ressar, H., Carlsson, M., Mõttus, V., Enel, M., Mardla, A., Täht, K.* The Geochemical Atlas of the Humus Horizon of Estonian Soil. – Tallinn – Uppsala, 1997. 75 p.
26. *Stark, J., Redente, E.* Trace element and salt movement in retorted oil shale disposal sites // J. Environ. Qual. 1986. Vol. 15. P. 282–288.
27. *Cornelis, G., Johnson, C. A., Van Gerven, T., Vandecasteele, C.* Leaching mechanisms of oxyanionic metalloid and metal species in alkaline solid wastes. A review // Appl. Geochem. 2008. Vol. 23, No. 5. P. 955–976.

Presented by V. Oja
Received October 19, 2009