Active filtration of phosphorus with hydrated oil-shale ash in constructed wetlands: geochemical modelling and phosphorus removal efficiency

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Kerogenous Oil-shale used at Estonian thermal power plants is a solid fuel of low energetic value. More than 95% of power production in Estonia relies on the use of oil-shale and about 45-50% of oil-shale remains after combustion as calcareous ash. The ash is rich in free lime (CaO) and anhydrite (CaSO4), with an Al-Si glass-like phase and secondary Ca(Mg)-silicate minerals [1]. The ash is hydraulically transported to large open plateaus, and due to hydration reactions forms a variety of secondary Ca-minerals ettringite, portlandite, Ca-aluminates and calcite. More than 280 million tons of ash is deposited and these dumps are considered as point source of contamination which almost completely lacks any further use.

Recent studies [2] [3] have shown a large potential of Estonian oil-shale fly ash and the hydrated ash sediment as an alternative media for phosphorous (P) removal in constructed wetland systems via active filtration through the alkaline media. The active filtration technique uses the direct immobilization of phosphates into low soluble forms and extensive super-saturation of pore-water is required for the precipitation of stable Ca-phosphate phases.

We studied the phosphorus binding capacity of hydrated oil shale ash in onsite pilot-scale experiment (with subsurface flow filters) in Estonia, using pre-treated landfill leachate (median P 3.4 $mg \cdot L^{-1}$) for a total of 12 months. The results show efficient P removal (median removal of phosphates 99%) in filters. The P removal efficiency of the hydrated ash increases with increasing P loading, suggesting direct precipitation of Ca-phosphate phases.

A computer programme Geochemist's Workbench was employed to calculate the saturation-index (SI), according to the data obtained from the experiment, with respect to hydroxyapatite (HAP) and Ca-minerals in ash (e.g. ettringite, portlandite). The SI values for the different Ca- minerals were between -2 to -12, indicating dissolution of these minerals. and thus providing Ca^{2+} ions to the pore-water.Especially ettringite (with average SI= -6.5) is most important mineral providing Ca^{2+} ions for the precipitation of HAP. The SI values for HAP were more than 8 during all the experiment.

[1] Kuusik *et al.* (2005) Characte rization of oil shale ashes formed at industrial-scale CFBC boilers. *Oil Shale* **22**, 407e 421. [2] Vohla *et a.* (2005) Alternative filter media for phosphorous removal in a horizontal subsurface flow constructed wetland. *J. Environ. Sci. Health*, **A40**, 1251 –1264. [3] Kaasik *et al.* (2008) Hydrated calcareous oil-shale ash as potential filter media for phosphorus removal in constructed wetlands. Water Res. **42**, 1315-1323.

Precambrian palaeosol from Baltica – reconstructing the Neoproterozoic climate

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Precambrian palaeosol profiles provide important and direct evidence for early weathering conditions reflecting the past climate (temperature, precipitation), atmospheric composition (pCO_2 , pO_2) and (microbial)biota. In this contribution we study a well-preserved Neoproterozoic weathering crust that is widespread under the Ediacaran-Phanerozoic sedimentary cover at the southern margin of the Baltic Shield, Baltic Basin.

The palaeosol marks an unconformable contact of peneplained Palaeoproterozoic – Mesoproterozoic metamorphic-plutonic rocks and overlaying unmetamorphosed Ediacaran sandstones –claystones. Palaeosol profiles were developed on rapakivi granites, sillimanite-cordierite and biotite-amphibole gneisses, amphibolites in the northern part and pyroxene and amphibole gneisses in the southern part of the area. The maximum age of the palaeosol is estimated at 1.3-0.8 Ga by the age of major denudation in Fennoscandia and the minimum age is defined by the age of overlying Ediacaran terrigenous sediments estimated at 600 Ma, which suggest that the age of weathering falls into the period of final stage of atmosphere oxygenation during Cryogenian.

Palaeosol is accessed in more than 100 drillcores where the thickness of the alteration profiles varies from few meters to exceptional 152 m on fractured-faulted sections of alumo-gneiss parent rocks. Palaeosol is preserved unmetamorphosed, but probably slightly modified by diagenetic illitization.

Palaeosol profiles are characterized by well-developed alteration zones grading gradually from (lateritic?) kaolinitic zone (kaolinite content 30-40wt%) to smectite-illite/smectite and chlorite(illite)smectite zones and into saprolite and fresh basement rocks. Chemical Index of Alteration (CIA, [1]) reaches values >90(95) in the uppermost parts of the alteration profiles. The Ti/Al ratios from parent rock into uppermost kaolinitized laterite are in most profiles constant at ~0.04-0.06 or 0.15-0.17 depending on host rock composition, suggesting *in situ* formation of profiles. Several profiles are characterized by Fe accumulation (Fe₂O_{3tot} are as high as 20%.) in the zone below strongly kaolinitized upper part of the palaeosol.

The quantitative weathering indicators suggest intense weathering in well drained landscapes under humid and warm conditions, with mean annual precipitation estimated at 1500-1800 mm/yr. This interpretation well agrees with palaeoposition of the Baltica continent at equator at the transition from Mesoproterozoic to Neoproterozoic [2], but there is no indication of global Snow Ball Earth glaciations that are believed to have occurred in the same period at about 710 and 635 Ma [3].

[1] Nesbitt and Young (1982) Nature 299, 715-717 [2] Cocks and Torsvik (2005) Earth Science Reviews 72, 39-66. [3] Hoffman et al. (1998) Science 281, 1342-1346.