

Graptoliit-argilliidi leostuvus merevees ja sellest tulenev keskkonnoahtlikkus.

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Magistritöö eesmärkideks oli anda ülevaade graptoliit-argilliidi (GA) niisutamisel mereveega välja leostuvatest elementidest, tilkvee pH, TDS, soolsuse ja temperatuuri muutustest ja katsekuhjaga toimuvatest protsessidest. Selle magistritöö jaoks ehitati unikaalne katseseade, mis hoidis 10 kg purustatud GA massi kogumiskasti kohal. Katsesekuhja kasteti iga nädal 1-5 korda seitsme ja poole kuuvälitel. Katsekuhja kastmisel koguti GA massist nõrguva tilkvee päevased ja nende summamana nädala keskmised tilkvee koondproovid. Igal päeval ja nädala keskmisel proovil mõõdeti pH, TDS, soolsus ja temperatuur. Edasi need proovid filtreeriti ja hapendati kontsentreeritud HNO_3 ning analüüsiti elementkoostis ICP-MS analüsaatoriga. Viie kuu möödudes katse algusest koguti kaks proovi katsekuhjalt ja kolm proovi katsekuhja sisemusest. Need tahked proovid määrati XRF ja XRD analüsaatoritel.

Tulemustest selgus, et tilkvesi muutub kiiresti happeliseks, püüdes terve katseperioodi ligikaudu vahemikus pH 2-2,50. Peale üheksandat proovi ületasid TDS ja soolsus pHmeetri mõõtepiiri 14,00 ppt. Orgaanikasisaldus kogutud proovides oli keskmiselt 16 % (LOI 500). Katsekuhjast leostus jälgelementidest suurtes kogustes V, U, Mo ja Ni. Põhielementidest leostus palju K, Mg, Na ja Al. Huvipakkuvalt palju Ni kontsentreerus porsumisel kollakasvalgesse sademesse katsekuhja pinnal. Leostumisprotsessi graafikuid analüüsides selgus, et GA terakestel on nõ pinna kile, mis takistab elementidel eralduda. Süsteemsel ja korduval kastmisel, pinnakile murdub ja leostumisprotsess on väga aktiivne. Kastmise katkemisel ja katsekuhja kuivades on protsess tagasipöörduv.

Tulemustest lähtuvalt on GA on küllastunud raskemetallidega ja pideva niiskusega kokkupuutel on GA kergesti murenev ja leostuv. Sellest tulenevalt on ilmastikutingimustele avatud GA keskkonnale ohtlik nii lasundis, kui aherainepuistangus.

Märksõnad: Graptoliit-argilliit, leostumine, mustad kildad, jälgelemendid, keskkonna ohtlikkus

Graptolite-argillite leaching in seawater and its possible results in environmental hazards.

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This Master's thesis first objective was to provide an overview of elements leaching from graptolite-argillite when watered with seawater. Secondary objective was to monitor pH, TDS, salinity and temperature changes in the graptolite-argillite experiment pile. Third objective was to describe changes in the graptolite-argillite experiment pile.

A special experiment device was built to keep 10 kg of crushed graptolite-argillite in a net basket overlaying the collection box. Experiment pile was watered for 1-5 times a week for seven and a half month. After watering the pile only the leaching water that was dripping from the pile was collected. From each sample pH, TDS, salinity and temperature was measured. Samples from one week formed an average weekly sample. The same parameters were measured. All average weekly samples were filtered, acidified with concentrated HNO_3 and analyzed with ICP-MS. Five months after the experiment beginning two samples were collected from the top of the pile and three samples from inside of the pile. These solid samples were analyzed by XRF and XRD.

The results showed that the leaching water quickly becomes acidic. PH stayed in the range of 2 to 2,50 for the entire experiment time. After the ninth sample TDS and salinity exceeded the pH meter measuringrange of 14.00 ppt. Organic content in the samples was an average of 16 % (LOI 500). Large amount of trace elements, such as vanadium, uranium, molybdenum and nickel was leached from the graptolite-argillite experiment pile. Also large amount of major elements like potassium, magnesium, sodium and alumina was leached out. By chemical weathering nickel concentrated in the yellowish precipitation material on the surface of the pile. After analyzing the leaching graphs it showed that GA has some kind of surface layer that prevents the elements from leaching. By watering graptolite-argillite systematically and repeatedly that surface layer breaks and the leaching process is very active. If the watering stops and the pile dries out then the process is reversed.

Based on the results graptolite-argillite is saturated with heavy metals and the constant exposure to moisture makes graptolite-argillite easily leachable. Consequently, graptolite-argillite open to all weather conditions is hazardous to the environment.

Key words: Graptolite-argillite, leaching, black shales, trace elements, environmental hazard .