

## LEACHABILITY OF TRACE ELEMENTS FROM THE AGED AND FRESH SPENT SHALE DEPOSIT – A FIELD STUDY

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**Abstract.** *A field study of the leaching of trace elements from the upper soil layer of a spent shale deposit was carried out. The study was conducted by installing a set of samplers in both active and closed parts of the deposit. Leachates were analyzed for pH, conductivity and concentrations of elements by ICP-MS. The results indicated release of metals from both parts of the deposit. Among the elements Mo, Zn, Ni, Cu, Cr and V were most mobile. The highest concentrations of Mo (104 µg/l), Zn (80 µg/l) and Ni (76 µg/l) were found in leachates from the active part of the deposit.*

**Keywords:** *spent shale deposit, leaching, field study, trace elements, heavy metals.*

### 1. Introduction

Oil shale, commonly defined as a fine-grained sedimentary rock containing significant amounts of organic matter, is widely distributed around the world [1]. Increased attention has been lately paid to the use of oil shale for oil and energy production, as well as related environmental problems [2–6].

Estonia has long-term experience in the industrial use of oil shale [7, 8]. A significant part of oil shale excavated in Estonia is used for thermal processing (semi-coking or retorting) to produce oil [7–9]. According to the World Energy Council, in 2005, more than half of the total shale oil in the world was produced in Estonia [10]. During retorting, oil shale is heated in the absence of oxygen to the temperature at which kerogen is decomposed or pyrolysed into gas, condensable oil and solid residue [7, 8]. According to [7] two main industrial retort technologies have been used in Estonia: the

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Kiviter and Galoter retorting processes. The Kiviter thermal processing of oil shale in Estonia was started in 1924. Since 1980 the Galoter retorting process has been employed.

Due to the high mineral content of oil shale a significant amount of solid wastes, spent shale, is formed, which has been deposited close to the retorting plants [3, 8, 11]. Spent shale is considered as hazardous waste [12]. The deposition of huge amounts of spent shale may affect the surrounding environment due to the leaching of harmful constituents, including potentially hazardous trace elements [3, 8, 13]. Coupled hydrological, geochemical and biological processes may influence the fate and transport of pollutants in the disposal site [6, 9, 14, 15]. The extent of contribution depends on the properties of wastes and field conditions.

The effect of spent shale disposal sites on the surrounding environment is an important consideration in both the short- and long-term view. Taking into account the substantial amounts of deposited waste and possible environmental impact more comprehensive knowledge about the leaching behavior of aged and fresh landfilled wastes is needed.

However, data on the process of leaching in field conditions from waste disposal sites are sparse due to the practical difficulties and expenses involved in the full-scale monitoring of sites and surrounding aquifers [13, 16, 17]. Also, little is known about the role of inorganic colloids [18] in the transport of metals from the spent shale deposit into the surrounding environment. Therefore, for environmental and human health risk assessment and beneficial remediation/reuse of waste it is important to determine the leaching potential of a given spent shale deposit.

Analysis of field leachates from the uppermost layer of a given waste deposit may give reliable data on their behavior to adequately evaluate the environmental impact of the deposition site. For this purpose a low-cost field leachate sampling method is applied, which consists in collecting the infiltrate under gravity flow without disturbing the surface structure of the soil. A similar technique could also be used to investigate the behavior of pollutants in the other types of waste deposition sites [13, 19].

The objective of this study was to evaluate the actual leaching of selected elements, such as Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Ni, Pb, Rb, Sb, Sr, Tl, V and Zn, from the upper layer of the fresh and aged spent shale deposit. The metals were selected due to their potential risk to the environment and human health. For that purpose sets of samplers were placed in both deposition fields during a one-year period.

## **2. Materials and methods**

### **2.1. Sampling**

The studied spent shale deposition field of Viru Keemia Grupp AS is located in Kohtla-Järve, Northeast Estonia. The deposit consists of a closed site (aged) and active site (fresh), which is currently in use. The aged spent shale

dump is partly covered with sparse grass and characterized by a relatively soft upper layer of 20–30 cm thickness and solid compacted matter in deeper layers [20].

Three sampling points were situated in the closed and three in the active site of the deposit. The distance between the active and closed sites was approximately 200 m. The sampling points in the closed deposition site were situated at a 10–30° slope triangularly at a 3–5 m distance from each other. In the fresh spent shale deposition site the sampling area was flat and samplers were placed on a 10 m<sup>2</sup> area. The samplers were installed by excavating a pit into the spent shale massive and pressing the sampler into the bank 15–20 cm below the surface, leaving the soil beneath undisturbed (Fig.). Each sampler was connected via a Teflon pipe to a one-liter polyethylene bottle for collecting the leachate.

After installation the pit was refilled with the excavated material and marked. The samplers were then left to collect drain water freely. Leachate samples were taken by opening the pit, changing the bottle and refilling the pit five times during the sampling period. The bottles were kept in a thermo box during transportation. The pH and conductivity (EC) of leachates were determined immediately after arriving in the laboratory. Samples for metal determination were kept in a refrigerator and analyzed later.

Sampling was conducted five times. In addition to liquid samples also solid samples from fresh and aged spent shale sampling areas were taken and analyzed for elements by ICP-MS.



Fig. Installation of a sampler at the closed site of the spent shale deposit.

## 2.2. Climate data

Meteorological data during the sampling period were obtained from the nearest, Jõhvi meteorological station of the Estonian Meteorological and Hydrological Institute (EMHI), which is located in Northeast Estonia. The monthly average precipitation varied from 13.9 to 159.5 mm and the monthly average temperature from  $-7.5$  °C to  $18.1$  °C during the field study.

## 2.3. Spent shale characteristics

Spent shale has variable composition because of differences in raw oil shale composition and the technological processes involved in oil production [7, 8, 21]. Calcite, dolomite, quartz, K-feldspars and clay minerals are dominant in the mineral part. Spent shale also contains easily soluble inorganic components and trace elements, which are hazardous to the environment and human health [8]. Table 1 presents concentrations of selected metals in raw oil shale and spent shale samples obtained from the literature and determined in the current study.

## 2.4. Analysis

Samples of fresh and aged spent shale (á 0.25 g) were digested in 3.5 mL (4.9 g) concentrated  $\text{HNO}_3$  (Scan Pure grade) using a Multiwave 3000 microwave oven (Anton Paar, Austria) with a program running at 1000 W for 1 minute followed by 350 W for 10 minutes. The digested samples were diluted with distilled water to 0.1 M  $\text{HNO}_3$  in a separate vessel to a final volume of 460.8 mL. The samples were then decanted to 14 mL polypropylene tubes for further analysis by ICP-MS (Thermo Element 2, Germany).

The following parameters of leachates were determined: pH, conductivity (EC) and concentrations of Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Ni, Pb, Rb, Sb, Sr, Tl, V and Zn. The pH and EC were measured using a BENCH PC 510 pH/Conductivity Meter (Eutech Instruments Pte Ltd, Singapore/Oakland Instruments, Vernon Hills, IL, USA). The leachates were preserved with 0.1 M  $\text{HNO}_3$  and analyzed directly by ICP-MS (Thermo Element 2, Germany). Blank tests without sample but applying the same procedure were carried out in parallel for each set of analyses.

**Table 1. Concentrations of selected metals, mg/kg, in raw oil shale sample, fresh spent shale (semi-coke) and aged spent shale (Kohtla-Järve, Northeast Estonia) samples**

Element	Raw oil shale <sup>a)</sup>	Fresh spent shale <sup>a)</sup>	Fresh spent shale <sup>b)</sup>	Rel SD, %	Aged spent shale <sup>b)</sup>	Rel SD, %
Ca	159 000	168 500	217 100	3	296 300	0.4
Fe	18 500	55 650	24 000	3	35 000	2
K	8 500	44 556	6 160	0.2	6 500	2
Mn	214	385	340	3	458	2
Ba	45	n.d.	80	3	125	2
Zn	27	37	17	3	29	1
V	19	34	26	5	39	1
Pb	19	42	41	3	69	1
Cr	15	43	24	5	34	1
Ni	13	23	20	4	30	0.2
Cu	6	11	19	3	43	0.1
Mo	3	5	2	3	3	2
Co	2.6	n.d.	3.4	3	5.2	3
Sb	0.3	n.d.	n.d.		n.d.	
Cd	0.2	0.1	0.1	6	0.1	5
Tl	n.d.	n.d.	0.3	2	0.5	1

n.d.: not determined

a) Saether et al., [8]

b) determined by ICP-MS in the current study.

### 3. Results and discussion

#### 3.1. pH and EC of field leachates

The general characteristics of field leachates from the active and closed parts of the spent shale deposit are given in Table 2. The values of pH and EC of leachates varied significantly. The pH values for leachates from both parts of the deposit were in the alkaline region. The results indicated great difference in EC values between the leachates from the active and closed parts of the deposit. The amount of dissolved inorganic compounds was significantly lower in the leachates from the closed part of the deposit.

The results also revealed a significant impact of meteorological conditions as well as the location of samplers on the leaching of matrix components. The values of pH and EC are presented in Table 2. Higher pH and EC values were found for leachates collected in heavy precipitation.

Pearson's correlation was performed between the precipitation, pH, EC and metals concentration in the collected leachates from the fresh and aged spent shale deposit (Tables 3 and 4). Good correlation was found between pH and EC, as well as between EC and alkaline metals concentration in the leachates from fresh spent shale (Table 3). Precipitation data correlated significantly with pH in the leachates from the aged matter (Table 4).

**Table 2. The values of pH, conductivity (EC,  $\mu\text{S}/\text{cm}$ ) and concentration of selected elements,  $\mu\text{g}/\text{l}$ , in leachates from the active (fresh) and closed (aged) sites of the spent shale deposit**

Parameter	Range (median)	
	Active site (n = 8)	Closed site (n = 9)
pH	7.4–11.5 (9.6)	7.3–10.6 (8.3)
EC	4200–7460 (5660)	678–4070 (2336)
Ca	556 350–967 100 (786 100)	19 800–626 500 (346 400)
Mg	12 300–172 600 (108 300)	70–74 700 (38 000)
K	133 700–894 000 (500 000)	55 900–153 500 (110 700)
Sr	1310–4380 (2900)	650–1 610 (1180)
Rb	230–1580 (870)	110–430 (220)
Mo	58–104 (95)	15–76 (42)
Ba	36–137 (80)	26–109 (52)
Ni	5.8–76 (62)	1.49–68 (22)
Sb	0.3–1.0 (0.6)	0.3–0.9 (0.6)
Tl	0.1–0.3 (0.2)	0.01–0.05 (0.03)
Cd	0.2–0.4 (0.2)	<0.02–0.4 (0.1)
Co	0.1–5.1 (2.2)	0.08–1.01 (0.3)
Cr	1.1–7.6 (5.5)	1.03–6.22 (3.8)
Cu	1.2–9.7 (4.3)	2.4–8.87 (4.9)
Fe	4–54 (32)	1.73–30.4 (13.4)
Mn	0.8–5.0 (1.7)	<0.02–1.6 (0.8)
Pb	0.01–3.9 (1.5)	0.1–1.6 (0.4)
V	1.0–3.8 (2.4)	0.2–5.8 (3.1)
Zn	1.1–80 (41)	3.66–92 (35)

n – the number of samples.

### 3.2. Leaching of metals

Concentrations of potentially harmful trace elements in field leachates from aged and fresh deposition fields are presented in Table 2. Leachates from the closed part of the deposit contained similar concentrations of Cu, lower concentrations of Co, Cr, Mo, Ni, Pb, Zn, and slightly higher concentrations of V compared to leachates from the active part of the deposit. Among the elements under study, Mo, Zn, Ni, Cu, Cr and V were the most mobile. The average concentrations of metals in leachates from the closed part of the deposit decreased as follows: Mo > Ni  $\cong$  Zn > Cu  $\sim$  Cr > V. In case of leachates from the active part of the deposit the concentration of elements decreased in the following order: Mo > Ni > Zn > Cr > Cu > V. The highest concentration of Mo (104  $\mu\text{g}/\text{l}$ ), Zn (80  $\mu\text{g}/\text{l}$ ) and Ni (76  $\mu\text{g}/\text{l}$ ) were found in leachates from the active part of the deposit. Remarkably, molybdenum exhibited the highest mobility although its absolute amount in spent shale is relatively small (Table 1). Among the other heavy metals, Ni had a relatively high concentration, while the concentrations of Pb and Cd were found to be almost negligible. A comparison of the average concentrations of the most mobile elements in leachates (Table 2) suggests that in the course of time the environmental pressure from Ni, Mo, Cr and Zn decreased and that from Cu and V slightly increased.

**Table 3. Pearson's correlation between selected parameters and elements concentration in leachates from fresh spent shale (bold with a significance level  $p < 0.05$ ). prec is precipitation data by EMHI**

	prec	pH	EC	Ca	Mg	K	Sr	Rb	Fe	Mn	Ba	Cd	Cr	Cu	Mo	Ni	Pb	Zn	Co	Tl	V
prec	1.00																				
pH	0.80	1.00																			
EC	-0.72	<b>0.95</b>	1.00																		
Ca	-0.78	<b>0.81</b>	<b>0.72</b>	1.00																	
Mg	-0.27	<b>0.97</b>	0.85	-0.45	1.00																
K	-0.77	<b>0.94</b>	<b>0.91</b>	<b>0.93</b>	<b>0.92</b>	1.00															
Sr	-0.81	<b>0.99</b>	<b>0.91</b>	<b>0.87</b>	<b>0.94</b>	<b>0.95</b>	1.00														
Rb	-0.77	<b>0.95</b>	<b>0.93</b>	<b>0.91</b>	<b>0.95</b>	<b>1.00</b>	<b>0.96</b>	1.00													
Fe	-0.64	<b>0.77</b>	<b>0.76</b>	0.47	<b>0.99</b>	0.62	0.60	0.65	1.00												
Mn	-0.39	0.70	0.65	<b>0.92</b>	n.d.	<b>0.91</b>	<b>0.92</b>	<b>0.91</b>	0.19	1.00											
Ba	-0.69	<b>0.87</b>	<b>0.87</b>	<b>0.91</b>	0.56	<b>0.97</b>	<b>0.86</b>	<b>0.97</b>	0.63	<b>0.89</b>	1.00										
Cd	-0.30	0.35	0.40	-0.02	<b>1.00</b>	0.24	0.39	0.26	0.26	-0.95	0.13	1.00									
Cr	-0.79	<b>0.98</b>	<b>0.90</b>	<b>0.74</b>	<b>0.93</b>	<b>0.87</b>	<b>0.96</b>	<b>0.89</b>	0.65	-0.11	<b>0.78</b>	0.49	1.00								
Cu	-0.69	<b>0.97</b>	<b>0.94</b>	0.65	<b>1.00</b>	<b>0.77</b>	<b>0.85</b>	<b>0.77</b>	0.40	-0.36	0.65	<b>0.74</b>	<b>0.81</b>	1.00							
Mo	-0.92	0.72	0.60	<b>0.78</b>	0.34	<b>0.76</b>	<b>0.73</b>	<b>0.75</b>	0.41	0.27	<b>0.73</b>	0.25	<b>0.73</b>	0.58	1.00						
Ni	<b>0.91</b>	-1.00	-1.00	-0.86	n.d.	-0.89	-0.89	-0.90	-0.51	-0.72	-0.90	0.60	-0.57	-0.36	-0.92	1.00					
Pb	-0.67	<b>0.96</b>	<b>0.94</b>	<b>0.70</b>	<b>1.00</b>	<b>0.89</b>	<b>0.94</b>	<b>0.91</b>	0.60	0.70	<b>0.81</b>	0.61	<b>0.94</b>	<b>0.91</b>	0.62	-0.80	1.00				
Zn	-0.74	<b>0.94</b>	<b>0.85</b>	0.62	<b>0.94</b>	<b>0.79</b>	<b>0.91</b>	<b>0.81</b>	<b>0.67</b>	-0.78	<b>0.68</b>	0.59	<b>0.98</b>	<b>0.81</b>	0.65	0.17	<b>0.93</b>	1.00			
Co	-0.77	<b>0.84</b>	<b>0.70</b>	<b>0.65</b>	0.55	<b>0.70</b>	<b>0.87</b>	<b>0.71</b>	0.40	-0.49	0.52	0.46	<b>0.87</b>	<b>0.81</b>	0.56	0.22	<b>0.79</b>	<b>0.86</b>	1.00		
Tl	-0.10	0.37	0.50	-0.06	0.78	0.25	0.19	0.28	0.62	-0.71	0.34	0.54	0.32	0.25	0.13	0.16	0.43	0.39	-0.09	1.00	
V	-0.76	<b>0.75</b>	<b>0.72</b>	<b>0.96</b>	-0.71	<b>0.90</b>	<b>0.77</b>	<b>0.89</b>	0.52	0.87	<b>0.93</b>	-0.12	<b>0.65</b>	0.50	<b>0.77</b>	-0.92	0.61	0.51	0.49	0.04	1.00

Table 4. Pearson's correlation between selected parameters and elements concentration in leachates from aged spent shale (bold with a significance level  $p < 0.05$ ). prec is precipitation data by EMHI

	prec	pH	EC	Ca	Mg	K	Sr	Rb	Fe	Mn	Ba	Cd	Cr	Cu	Mo	Ni	Pb	Zn	Co	Tl	V
prec	1.00																				
pH	<b>0.87</b>	1.00																			
EC	-0.24	0.02	1.00																		
Ca	-0.64	-0.82	-0.41	1.00																	
Mg	-0.51	-0.73	-0.82	<b>0.87</b>	1.00																
K	-0.43	-0.31	<b>0.96</b>	0.16	-0.10	1.00															
Sr	-0.43	-0.69	0.85	0.27	-0.07	<b>0.71</b>	1.00														
Rb	-0.25	-0.08	0.88	-0.24	-0.51	<b>0.81</b>	0.74	1.00													
Fe	-0.56	-0.30	-0.08	0.58	0.44	0.44	0.11	0.03	1.00												
Mn	-0.79	-0.60	0.65	<b>0.75</b>	0.65	0.53	0.31	0.18	0.66	1.00											
Ba	0.38	-0.89	0.05	0.08	-0.22	0.01	0.23	-0.13	-0.11	-0.42	1.00										
Cd	-0.15	0.05	-0.11	0.11	0.14	-0.13	-0.18	-0.39	0.44	0.15	0.30	1.00									
Cr	-0.29	0.19	-0.06	0.03	-0.01	0.06	0.30	0.38	0.14	0.18	-0.68	-0.40	1.00								
Cu	-0.49	-0.38	0.71	-0.09	-0.14	0.16	0.54	0.45	-0.27	0.07	-0.19	0.01	0.38	1.00							
Mo	-0.57	-0.70	-0.51	<b>0.95</b>	<b>0.92</b>	0.12	0.22	-0.28	0.56	<b>0.80</b>	-0.10	0.10	0.11	-0.13	1.00						
Ni	-0.64	-0.99	-0.29	0.51	0.53	-0.22	-0.29	-0.35	0.17	0.38	-0.18	0.37	-0.29	0.29	0.33	1.00					
Pb	-0.42	-0.55	-0.13	0.12	0.16	-0.20	-0.07	-0.15	-0.31	-0.08	-0.01	0.04	-0.30	0.51	-0.04	<b>0.86</b>	1.00				
Zn	-0.73	-0.62	-0.30	0.58	<b>0.65</b>	0.01	-0.11	-0.34	0.50	0.49	-0.14	0.59	-0.21	0.21	0.50	<b>0.87</b>	0.58	1.00			
Co	-0.38	-0.55	0.35	<b>0.68</b>	0.58	0.14	0.27	-0.07	0.35	<b>0.73</b>	-0.17	-0.16	0.22	-0.18	<b>0.78</b>	0.06	-0.18	0.07	1.00		
Tl	-0.58	-0.75	-0.41	0.43	0.55	-0.10	-0.10	-0.29	-0.02	0.26	-0.13	0.14	-0.33	0.35	0.33	<b>0.91</b>	<b>0.88</b>	0.03	0.03	1.00	
V	-0.30	-0.36	-0.98	0.53	<b>0.68</b>	-0.31	0.25	-0.36	-0.04	0.14	-0.40	-0.45	<b>0.83</b>	0.33	0.59	-0.05	0.06	0.15	0.33	0.22	1.00

The concentration ranges of most analyzed compounds in the leachate samples under study complied well with previously published data on landfill leachates [22–24]. The leaching of elements from both spent shale deposit areas depended on solid matrix properties and conditions in a given sampling site. Pearson's correlation analysis demonstrated a significant correlation between most trace elements and alkali and alkaline earth metals in leachates from fresh spent shale ( $p < 0.05$ ) (Table 3). Thus, the alkaline metals present in fresh spent shale exhibited similar leaching behavior. The absence of correlation between these metals in the leachates from aged spent shale means that leaching is controlled by complex geochemical factors (Table 4).

In leachates from the closed part of the deposit a significant correlation was observed between Mo and Ca, K, Sr, Rb, Ba, Cr and V. A positive correlation between Ni and precipitation ( $p < 0.05$ ) was found. Zn correlated with Fe, Ba, Cr, Cu and Pb, Cu correlated with Cd and Cr. Correlation between V and elements Mn, Cr, Mo and Ni was observed. In the case of leachates from the closed part of the deposit there was a good correlation between Mo and Ca, Mg, Mn, and a positive correlation between Mo and Fe (Table 4). Also, correlation between V, Zn and Mg, Ni and Cr was established.

The obtained data suggest that soluble Ca, Fe and Mn containing components, i.e. inorganic colloids, play a significant role in the transport of trace elements from the spent shale deposit. As is known, metals bind to the colloidal matter present in the leachate and groundwater [18, 22–28]. When associated with colloids, metals show significantly different transport properties compared to dissolved metals. In soils and aquifers, mobile colloidal particles originate mostly from in situ generation of submicron-sized mineral and organic matter particles, which are present naturally [24–26]. Such particles may be composed of clay minerals, mineral precipitates (e.g. Fe, Al, Mn, or Si oxides and hydroxides, carbonates, phosphates), organic biopolymers (e.g. humic and fulvic acids, polysaccharides, etc.) and biocolloids [23]. Colloids in disposal sites reflect the waste composition and degradation [22–24]. Based on literature data [18, 22–28] and characteristics of spent shale we also assume a significant role of inorganic colloids in the transport of metals in waste disposal. According to [28] mobile colloids can be generated by a number of mechanisms, including precipitation of colloidal size phases, dissolution of cementation agents composed of fine-grained crystalline and poorly crystalline secondary minerals, and release from materials via physicochemically controlled dispersion processes.

Although the concentrations of elements in field leachates are below permissible limits, the spent shale deposit may represent a constant source of potentially hazardous elements [29, 30], particularly Mo, Ni and Zn. In [29] increase of Mo concentration in plants growing on retorted oil shale disposal piles was observed. Rooney and coauthors [30] demonstrated that with increasing pH of soil solution soluble Ni became more toxic to plants.

Thus, leaching characteristics of waste matter in a given disposal site need to be taken into account by phytoremediation of the solid waste deposit.

#### 4. Conclusions

The deposition and subsequent hydration of the spent shale deposit did not lead to a complete immobilization of harmful substances. The estimation of the risk derived from extensive waste deposition requires better knowledge about the real leaching potential of the waste massive.

Results revealed that colloids can be involved in the transport of metals in waste disposal.

Potentially hazardous compounds may migrate to environmental media for a long time.

The present study demonstrates a possibility of evaluating the environmental impact of a solid waste deposit using a simple and effective low-cost field sampling method.

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