

LEACHING BEHAVIOUR OF OIL SHALE SEMICOKE: COMPLIANCE WITH THE WASTE ACCEPTANCE CRITERIA FOR LANDFILLS

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Besides strict requirements for landfills the EU has also established criteria and procedures for the acceptance of waste delivered to landfills. Hazardous waste landfilled must meet the relevant waste acceptance criteria, which, besides standards for physical stability, consist of quantitative limits for leachable substances and organic matter. Evaluated testing methods – batch tests and a percolation test – were used in this investigation to study the leaching behaviour of oil shale semicoke. The results obtained indicate that none of the leaching limit values for inorganic components were exceeded in the analysed semicoke samples. The influence of recarbonation on the leachability of different components from semicoke was also studied.

Introduction

Oil shale semicoke is a solid waste resulting from oil shale retorting and is classified as hazardous waste in the Estonian Waste List [1]. The Waste List currently valid in Estonia is based on the EU Waste List [2]. According to the general logic of the EU Waste List, wastes that have undergone the process of pyrolysis should be categorized as hazardous waste since they contain tarry and bituminous substances. Consequently, the oil shale semicoke, which is also a pyrolysis waste, has been classified as hazardous waste in Estonia. Bearing this in mind, a major task is to bring the landfills for semicoke disposal into compliance with the requirements of the European Union. According to the EU regulation [3] landfills are divided into three main categories: hazardous, non-hazardous and inert waste. Each category has strict requirements on the properties of waste which may be deposited in

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these landfills. Stable non-reactive hazardous wastes may meet the criteria for their placement in non-hazardous waste landfills within the cells for inorganic waste with low organic/biodegradable content [3].

To be able to establish whether a waste will meet the relevant waste acceptance criteria and determine which criteria the landfill for semicoke must fulfill there is an inevitable need to investigate the composition of semicoke, i.e. the total organic carbon (TOC), and to analyse leaching of semicoke in accordance with the EU requirements. Up to now no systematic study has been carried out to evaluate the semicoke leaching characteristics according to the regulatory criteria of the EU. Data have been published on the extremely high pH value (approx. 12) of leachate or eluates of semicoke and high concentrations of different ions (i.e. sulphide, sulphate) in the eluates of semicoke [4].

The results from more thorough leaching studies can be found for retorted Rundle oil shale (Australia) [5, 6] and Green River Formation oil shale (USA) [7]. Unfortunately, the leaching behavior of different retorted oil shales is not strictly comparable because of the dependence on the raw shale mineralogy, the retorting process, etc. The first articles about leaching behavior of Estonian oil shale thermal treatment wastes – particularly ashes generated by oil shale combustion – deal with leaching of polycyclic aromatic compounds [8, 9]. Recently a paper on speciation of sulphur species in oil shale semicoke leachate has been published [10].

Leaching is typically assessed using short-term leaching tests. In most cases such tests cannot provide satisfactory estimates of leaching in long perspective taking into account the changes occurring due to the weathering and ageing when specific landfilling procedures are used. Since recarbonation affects leaching of different components, using the test data of the initial highly alkaline samples may lead to misestimating the leaching of semicoke in the natural environment.

The objective of this work was to carry out leaching tests and determine the composition of semicoke eluates in accordance with the requirements of the legislation. In addition, the changes in the leaching behavior of semicoke after recarbonation in laboratory experiments were investigated.

Materials and methods

Oil shale semicoke samples studied in the present work were obtained from the shale oil producing company *Kiviõli Keemiatööstus*, Estonia. The samples were collected from the retort hydrolock outlet as subsamples of 1 kg and mixed together into one composite sample (12–13 kg). Since the Kiviõli plant utilizes only partly enriched oil shale for shale oil production, the waste contains considerable amounts of limestone. The particle size distribution of the semicoke from the process was studied; the majority of the larger particles (>5 cm) in the waste material consists of

limestone. These limestone fragments were not incorporated into the composite sample.

Elements present in the semicoke samples were determined by inductively coupled plasma spectroscopy (ICP-AES) according to the accredited method used in the environmental analysis laboratory of *Tartu Keskkonnauuringud*.

In order to characterize the organic residue, the semicoke samples were analyzed for Fischer assay oil yield and extracted with benzene-ethanol mixture (4:1) in a Soxhlet apparatus. The total organic carbon (TOC) analysis was performed by *Tartu Keskkonnauuringud*.

The leaching of the semicoke samples was performed according to the Estonian standards EVS-EN 12457 and CEN/TS 14405:2004. The tests performed were compliance tests for leaching of granular waste materials and sludges and a leaching behavior test, respectively. The compliance tests were one-stage batch tests with distilled water at a liquid to solid ratio of 10 l/kg and 2 l/kg. The leaching behavior test applied was an up-flow percolation test. Semicoke with a particle size of <10 mm without size reduction was used in all leaching tests. Test portions of 110 g and 600 g (dry weight) of semicoke were used for the eluate preparation in the batch tests. The percolation test was performed with 780 g (dry weight) of semicoke using a column with the diameter of 5.9 cm and the height of 40 cm. From the percolation test the eluate fraction corresponding to L/S ratio of 0.1 l/kg was collected and analysed.

In the recarbonation experiments imitating natural recarbonation the semicoke samples were exposed to the atmospheric air in laboratory conditions at a room temperature for about 3 weeks. The pH of the leachate of the samples was approximately 11.5 after the exposure. In order to enhance the recarbonation, the semicoke samples were kept in the atmosphere of CO₂ for 3 days. The pH of the leachates of the CO₂-treated samples was around 8.

The eluates were analysed using standard methods approved for water analysis. Elements present in the eluates were analysed at *Tartu Keskkonnauuringud* using the ICP-AES method. Dissolved organic carbon (DOC) values in the eluates were measured using Dr. Lange cuvette tests for TOC analysis (LCK 381). Sulphates were analysed by Dr. Lange cuvette tests (LCK 353) or by ion chromatography (*Tartu Keskkonnauuringud*). Chlorides and fluorides were analysed by ion chromatography (*Tartu Keskkonnauuringud*).

Results

The element concentrations in two solid semicoke samples are presented in Table 1. The contents of organic compounds in semicoke are provided in Table 2. Approximately 20 semicoke samples from the *Kiviõli Keemia-*

tööstus were analysed for their organic residue. The following comparison was made on the basis of the above investigation (unpublished data). An extraordinarily high content of organic compounds was found in sample 25 of the semicoke. In contrast, sample 27 had quite a low content of organics and in general had the characteristics similar to the average obtained by analysing several semicoke samples from the *Kiviõli Keemiatööstus*. Analysis also showed (Table 2) that TOC values for oil shale semicoke exceeded the waste acceptance criteria for landfills. The application of TOC values for the characterization of organic carbon residue in semicoke will be presented in a separate article (manuscript in preparation).

Table 1. Element content in oil shale semicoke samples

Element	Concentration, mg/kg	
	sample 25	sample 27
Ca	250000	250000
Mg	9800	12000
Fe	27000	25000
Na	990	1100
K	7300	8800
Al	12000	16000
As	10	10
Ba	44	54
Cr	16	18
Cu	7	10
Mn	190	230
Mo	3.9	4.5
Ni	16	17
Pb	45	39
Se	<5	9
Zn	12	13
Cd	nd	<1
Hg	nd	0.03
Sb	nd	<5
Sr	nd	300
S _{total}	38000	28000

nd – not determined

Table 2. Parameters characterizing organic residue in oil shale semicoke samples

Parameter	Values	
	Sample 25	Sample 27
Fischer oil, %	3.1	0.3
Yield in Soxhlet extraction, g/kg	16	2
TOC, %	11.3	8.1

Semicoke composition (Table 1) strongly resembles the composition of raw oil shale as it contains high amounts of Ca, Mg, Fe, Al, K and Na. However, the concentrations of various metals and semi-metals, which are important due to their environmental hazardousness and leaching limit values, are comparatively low in the semicoke.

Tables 3 and 4 compare data from leaching tests recommended by the EU as standard leaching tests for granular waste.

Table 3. Amount of constituents leached from semicoke in batch leaching tests and leaching limit values for hazardous waste acceptance at landfills for hazardous (Haz) and non-hazardous (Non-haz) wastes

Compo nents	L/S = 10 l/kg				L/S = 2 l/kg			
	Leaching limit values, mg/kg		Amount leached from semicoke, mg/kg		Leaching limit values, mg/kg		Amount leached from semicoke, mg/kg	
	Haz	Non-haz	Sample 25	Sample 27	Haz	Non-haz	Sample 25	Sample 27
Ca	–	–	13000	9800	–	–	10000	4400
Mg	–	–	0.22	0.17	–	–	0.2	0.09
Fe	–	–	<0.2	<0.2	–	–	nd	nd
Na	–	–	150	230	–	–	118	188
K	–	–	550	1700	–	–	820	1880
Al	–	–	0.35	<0.2	–	–	0.062	nd
As	25	2	<0.1	<0.1	6	0.4	nd	<0.1
Ba	300	100	1.7	3.1	100	30	1.8	1.9
Cd	5	1	nd	nd	3	0.6	nd	nd
Cr (total)	70	10	<0.2	<0.2	25	4	nd	nd
Cu	100	50	<0.2	<0.2	50	25	nd	nd
Hg	2	0.2	nd	nd	0.5	0.05	nd	nd
Mn	–	–	<0.2	<0.2	–	–	nd	nd
Mo	30	10	0.8	0.44	20	5	0.64	0.22
Ni	40	10	<0.2	<0.2	20	5	nd	< 0.2
Pb	50	10	<0.2	<0.2	25	5	nd	<0.2
Se	7	0.5	nd	<0.5	4	0.3	nd	nd
Zn	200	50	<0.2	<0.2	90	25	nd	nd
Sb	5	0.7	nd	<0.5	2	0.2	nd	<0.5
Sr	–	–	nd	51	–	–	nd	nd
S _{total}	–	–	11000	4600	–	–	11600	4200
DOC	1000	800	390	40	480	380	450	nd
SO ₄ ²⁻	50000	20000	740	860	25000	10000	260	nd
Cl ⁻	25000	15000	1800	2100	17000	10000	4600	nd
F ⁻	500	150	<5	nd	200	60	nd	nd
TDS	100000	60000	47500	32000	70000	40000	38000	20100

nd – not determined, elements that were not present in the solid semicoke samples in amounts exceeding the leaching limits

“–“ no set leaching limit values

Table 4. Concentrations of constituents in the eluate (at L/S =0.1 l/kg) from the up-flow percolation test and respective leaching limit values for hazardous waste acceptable at landfills for hazardous (Haz) and non-hazardous (Non-haz) waste

Components	Leaching limit values, mg/l		Co, mg/l
	Haz	Non-haz	Sample 27
Ca	–	–	1500
Mg	–	–	nd
Fe	–	–	<0.02
Na	–	–	190
K	–	–	2700
Al	–	–	0.05
As	3	0.3	<0.1
Ba	60	20	1.3
Cd	1.7	0.3	nd
Cr	15	2.5	<0.02
Cu	60	30	nd
Hg	0.3	0.03	nd
Mn	–	–	<0.02
Mo	10	3.5	0.12
Ni	12	3	< 0.02
Pb	15	3	<0.02
Se	1	0.15	<0.05
Zn	3	0.2	nd
Sb	60	15	<0.05
Sr	–	–	35
DOC	320	250	73
SO ₄ ²⁻	17000	7000	150
Cl ⁻	15000	8500	nd
F ⁻	120	40	nd

The leaching limit values for hazardous waste calculated at L/S 10 l/kg and 2 l/kg for total release are presented in Table 3 and expressed in mg/l for the first eluate of percolation test at L/S 0.1 l/kg in Table 4. The high pH (12.3–12.6) which is characteristic of the eluates of fresh semicoke is also worth mentioning.

It can be seen from Table 3 that the quantities of different components leaching from the semicoke vary depending on the various L/S ratios applied in the batch tests. The main parameter determining the leaching amounts of components is their solubility in water. The latter can be also concluded by comparing the leached amounts presented in Table 3 with the data in Table 1 showing the total amount of different elements in the semicoke samples. The fact that the leaching was below the allowed limit in both the batch tests and the percolation test, may be important for practical reasons. The results show that it should be sufficient to perform one simple batch test for compliance testing of oil shale semicoke in everyday practice.

Comparison of the data from the semicoke leaching tests with leaching limit values (Tables 3 and 4) provides additional information for complying

with the construction requirements of landfills for semicoke disposal. Our results show that even more strict leaching limit values of inorganic components for hazardous waste which are acceptable at landfills for non-hazardous waste have not been exceeded. Further more, the concentration of Cu, Mo, Zn, Cd and Hg in the analysed semicoke samples was lower than the particular leaching limit values (Table 1). The only value in our study exceeding the mentioned criteria was the DOC value (one sample only). As mentioned previously, this sample was uncharacteristically rich in organic compounds compared to the average semicoke sample. We believe that this is most likely due to the incorrectly functioning or operating process and therefore is a worst-case scenario.

The leaching of major and minor components can be affected by changes caused by the weathering of waste during disposal. Evaluating the environmental consequences of landfilling of semicoke prompts to study the changes in leaching behaviour of semicoke during certain disposal scenarios. The effect of recarbonation on the leaching of constituents of semicoke is presented in Table 5. The pH of the semicoke leachates decreased due to recarbonation, and the conversion of metal hydroxides to carbonates took place. The pH of the leachates of the air exposed samples and the CO₂ treated samples decreased to 11.5 and to 8, respectively.

Table 5. Concentrations of constituents in the eluates and calculated fractions leached from the semicoke in batch leaching tests (L/S 10 l/kg) of untreated, air exposed and CO₂ treated semicoke (Sample 27)

Component	Untreated sample		Exposed to air		CO ₂ treated	
	mg/l	%	mg/l	%	mg/l	%
Ca	980	3.92	820	3.28	880	3.52
Mg	0.017	0.001	0.048	0.004	200	16.67
Fe	< 0.02		< 0.02		< 0.02	
Na	23	20.91	17	15.45	17	15.45
K	170	19.32	66	7.50	120	13.64
Al	< 0.02		0.71	0.04	0.037	0.002
As	< 0.01		nd		< 0.1	
Ba	0.31	5.74	0.08	1.48	0.026	0.48
Cr	< 0.02		< 0.02		< 0.02	
Cu	< 0.02		< 0.02		< 0.02	
Mn	< 0.02		< 0.02		0.054	0.23
Mo	0.044	9.78	0.049	10.89	0.092	20.44
Ni	< 0.02		< 0.02		< 0.02	
Pb	< 0.02		< 0.02		< 0.02	
Se	< 0.1		< 0.02		nd	
Zn	< 0.02		< 0.02		0.042	3.23
Sr	5.1	17.00	2.2	7.33	0.93	3.10
S _{total}	460	16.43	770	27.50	1700	60.71
SO ₄ ²⁻	86		333		1376	

Leaching of Ca, Ba, Sr detected for recarbonated samples was less than that of non-carbonated ones. Leaching of those components could decrease due to the formation of less soluble carbonates. Since $\text{Mg}(\text{OH})_2$ is much less soluble than MgCO_3 , the leaching of magnesium increases in the recarbonated samples.

The recarbonation of semicoke increased the leaching of Mn, Mo, Zn, total S and SO_4^{2-} . The mobilization of such critical components as Mo and Zn at lower pH values is not an issue, since their content in solid semicoke is already lower than the respective leaching limit. Recarbonation and accompanying pH change increased the release of sulphates from the solid semicoke. Similar effect in the case of municipal solid waste incineration residues has been explained as a result of increased solubility of secondary minerals, like ettringite, at lower pH values [11]. This can apply to the oil shale semicoke samples in which the formation of ettringite has also occurred [12]. Another reason could be the oxidation of sulphides during the recarbonation process.

Conclusions

Before landfilling, a quantitative information on the leaching properties of wastes to demonstrate a compliance with the appropriate waste acceptance criteria is required. Analysis of the eluates of oil shale semicoke showed acceptable leaching limit values for hazardous waste at a landfill for non-hazardous waste. The data presented confirmed that the leaching of heavy metals is not a problem in the case of oil shale semicoke. However, the results also indicated that the leaching of organic compounds may exceed the limit for DOC. This may result from an operational mistake during the retort process.

Besides the compliance with the acceptance criteria, the very high pH of the leachate of fresh semicoke and its evolution with time must be also considered. Recarbonation of the oil shale semicoke decreases considerably the alkalinity of it. In the long term, due to the atmospheric CO_2 , the proton activity in the semicoke leachates may increase by four orders of magnitude. During the landfilling the change in pH is probably one of the major factors affecting significantly the mobility of different components of semicoke.

We would also like to emphasize the importance of careful sampling since, typically, the largest uncertainty in the analysis is the heterogeneity of the waste material. It is essential to define the minimum quantity of the waste material to assess the landfill waste acceptance criteria below which variations in quality may be judged to be insignificant. Therefore, a higher value of a parameter, like the DOC for example, in a semicoke sample from one particular retort should not result in exceeding of the leaching limit of the composite sample which contains semicoke from 6–7 different retorts (working under optimal technological conditions).

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