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**Mineral composition of semi-coke deposits at Viru Keemia
shale-oil plant, Kohtla-Järve**

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Introduction

Estonia is the world's largest consumer of oil shale. The main oil shale utilization activities are electricity and heat generation and conversion to other forms of fuels (shale-oil, shale-oil gas). About 19% of all of the oil shale extracted annually is used for retorting shale-oil and shale-gas mostly as a by-product. Retorting of oil shale is accompanied with the huge amounts of environmentally hazardous solid retort residue – semi-coke. Production of 1 tonne of shale-oil is accompanied by the generation of almost 3 tonnes of semi-coke.

Two different retorting processes are used in Estonian oil shale chemical industry. The net oil yield efficiency is 11-17.5% and the amount of organics left in semi-coke is considerably higher (up to 16%, Tang *et al.*, 2003) compared to coal or oil based chemical industry. Residual organics (posing *in situ* ignition hazard) in semi-coke and leachates from it containing phenols, PAHs, oil products are main reasons for its harmful environmental effect. Retorting process of oil shale is also accompanied with the generation of organically contaminated condensate/pyrogenous water, fuses and several other toxic products. Another concern is high alkalinity of semi-coke leachates (Kahru & Põllumaa, 2006).

Finding ways for utilization of semi-coke is very important in the light of its environmental effects and increasing environmental taxes may render the shale oil production economically unprofitable. For decades from 1950's on semi-coke was mostly used in production of mineral wool and to a smaller extent in cement and compost production. Total mineral wool production from 1959 to 1985 was ~5.3 million m³, estimated share of total semi-coke in feed was 0.83 million tonnes (Veski, 2005). Today, small amount of semi-coke is used as an ingredient of composts (approx. 50%) in mixture with pig slurry and peat and for manufacturing rock wool and IVU blocks. Minor amount of semi-coke (10,000 t annually) has been used for cement production in *Kunda Nordic Cement Ltd*. But utilization of semi-coke in this way and amounts only mitigates the situation not resolving the problem. Several methods for

complete utilization of semi-coke have been proposed. Kuusik *et al.*, (2004) carried out an extensive study to find the most suitable energy and cost-effective methods for utilization of semi-coke as a fuel. The best way proposed is the combustion of semi-coke in mixture with small amount of oil shale in specially designed circulating fluidized bed (CFB) boilers at the place of waste formation and by adding it to the fuel in a certain proportion in cement clinker production (Kuusik *et al.*, 2004).

Environmental as well as the reusability aspects of the semi-coke depend besides of its organic material content also on the composition of semi-coke mineral matter. Although different aspects of Estonian oil shale, its geology, composition and use are well studied (e.g Kattai *et al.*, 2000), to our best knowledge there is no comprehensive study on the semi-coke mineralogy and the mineralogical composition of the semi-coke and its deposits is virtually unknown.

The objectives of this thesis are to study the:

- formation and stability of the semi-coke minerals during the partial thermal decomposition and subsequent reactions;
- transformation processes during the hydration of semi-coke under atmospheric conditions at the semi-coke waste heaps and plateaus;
- composition and spatial variation of the semi-coke sediments in waste heaps.

Origin and composition of oil shales

Oil shales are fine-grained sedimentary rocks that contain relatively large amounts (10-65%) of organic matter (kerogen) from which significant amounts of shale-oil and combustible gas can be extracted by destructive distillation (Energy Minerals Division, 2006).

Oil shales are found world-wide in all types of sedimentary rocks of Cambrian to Neogene age. Depending on their original depositional environment oil shales are divided into three basic groups: 1) terrestrial, 2) lacustrine, 3) subtidal or marine shales (Saether *et al.*, 2004). Variety of depositional environments of oil shales are reflected also in their mineralogical and geochemical composition and especially in the biotic derivation of their organic matter. Organic rich calcareous sediment - kukersite - found in sediments of Lower to Upper Ordovician age in Estonia and north-western Russia is a typical marine oil shale.

The organic matter of kukersite is composed mostly of kerogen with few percent of bitumen (Koel, 1999). It is considered to be of marine origin consisting almost entirely of accumulations of discrete bodies, telalginite derived from a colonial microorganism *Gloeocapsomorpha prisca* (Koel, 1999; Lille, 2002). However, Kattai *et al.* (2000) points out that the kukersite kerogen is more similar to lacustrine oil shales and sapropelic coals than the kerogen of marine oil shales.

Besides of organic matter kukersite contains significant amounts of carbonaceous and terrigenous matter. The last two constitute kukersite's mineral matter. The elemental composition of kerogen and the average chemical and mineral composition of the mineral parts are shown in Tables 1, 2 and 3.

Table 1. Elemental composition of kerogen, wt.% (Koel, 1999).

Organic part	
C	76.0-77.5
H	9.4-9.9
S	1.2-2.0
N	0.2-0.5
O	9.0-11.0
Cl	0.5-0.9

Table 2. Average chemical composition of kukersite mineral part, wt.% (Arro *et al.*, 1998).

Sandy-clay part (with crystal water)		Carbonate part	
SiO ₂	59.8	CaO	48.1
CaO	0.7	MgO	6.6
Al ₂ O ₃	16.1	FeO	0.2
Fe ₂ O ₃	2.8	CO ₂	45.1
TiO ₂	0.7		
MgO	0.4		
Na ₂ O	0.8		
K ₂ O	6.3		
FeS ₂	9.3		
SO ₃	0.5		
H ₂ O	2.6		

Table 3. Average mineral composition of kukersite mineral part, wt.% (after Utsal, 1984).

Mineral	wt%
Quartz	11
K-feldspar	7
Clay minerals	20
Calcite	43
Dolomite	13
Pyrite	6

On dry weight basis, oil shale consists of 10 to 65% of organics, 20-70% of carbonate minerals and 15-60% of terrigenous minerals (quartz, feldspars and clay minerals) (Kattai *et al.*, 2000). The major components of organic matrix are phenolic moieties with linear alkyl side-chains (Kahru & Põllumaa, 2006).

The content of carbon in the organic matter of kukersite is low (76.7%). Sulfur content is 1.6%. The moisture content is 9–12% and calorific value 8–10 MJ/kg, which is lower than that of the other fuels (as an example the average coal – 22.5 MJ/kg, natural gas – 33.5 MJ/m³, peat briquette – 16.5 MJ/kg (Gavrilova *et al.*, 2005).

The kukersite occurs in the area of about 5000 km² and it forms two large deposits (Figures 1, 2): (1) the *Estonian-Leningrad* deposit which is located in the north-eastern Estonia and north-western Russia. The productive seam thickness varies from 2.7-3.0 m in the northern part of deposit where it outcrops to surface, to 1.4-2.0 m in the southern and western parts where the seam is buried at 50-90 m depth; (2) the *Tapa* deposit which is situated south-west of the *Estonian* deposit with seam depth 60-170 m below the surface. The seam has maximum thickness of 2.0-2.3 m in the central part of the deposit. The Tapa deposit is not in use at the moment (Kattai *et al.*, 2000).

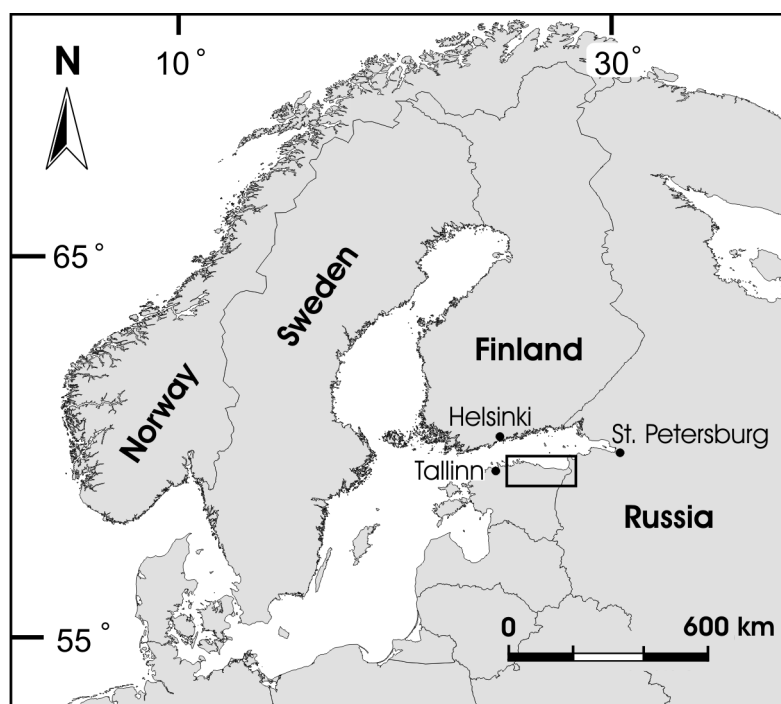


Figure 1. Location of Estonia and of the area containing the oil shales in Estonia and Russia, as detailed in Fig. 2.

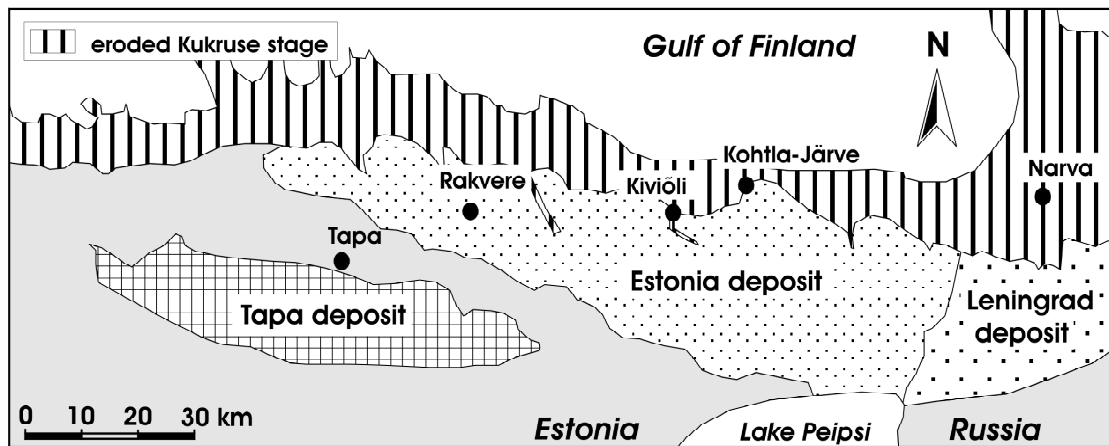


Figure 2. Geological sketch indicating areal distribution of the Estonian-Leningrad and Tapa oil shale deposits (after Bauert & Kattai, 1997)

The reserves of the Estonian deposits lying in the area of about 2000 km² make nearly $5 \cdot 10^9$ t, including $1.5 \cdot 10^9$ t of active reserves. To the present day, oil shale has been mined in the amount of about 10^9 t, whereas in the recent years $13\text{--}14 \cdot 10^6$ t of oil shale has been extracted *per annum* (Veiderma, 2003; AS Eesti Põlevkivi, 2006).

Ordovician section in North Estonia host in addition to kukersite oil shale also Lower Ordovician organic rich shales known as *Dictyonema Shale*. The *Dictyonema* shale occurs on an area of about 11,000 km² with the thickness of the seam 1–8 m. Reserves of this shale considerably surpass those of kukersite but the quality of the shale is poor: heating value 5–8 MJ/kg, oil yield (Fischer Assay) 3–5%, sulfur content 2–4%. This prevents their utilization for energy production and processing into oil (Koel, 1999).

Oil shale consumption

The Estonian kukersite is the largest oil shale resource in the world used industrially today (Bauert & Kattai, 1997). Oil shales have been known here since the 18th century and large-scale exploration for oil shale deposits and subsequent exploitation by continuous mining started already during the World War I (WW I). The main industrial activities using the oil shale resource are electricity and heat generation and conversion to other forms of fuels (shale-oil, shale-oil gas). Before and during the first years after the WW II, electricity production was a side-branch in the oil shale consumption as the preference was given to its processing into oil products and fuel gas, but today the oil shale is primarily used for electricity production at two large power plants – the Balti Power Plant (established in 1965) and the Eesti Power Plant (established in 1973) (Figure 3) The peak annual production (mining) of kukersite was 31 million tonnes in 1980. The mining of oil shale has decreased since that to 21.1 million tonnes in 1990 and 12.5 million tonnes in 1998 (Kattai *et al.*, 2000). During the last years the annual output of oil shale mining has stabilized around 13-14 million tonnes (AS *Eesti Põlevkivi*, 2006).

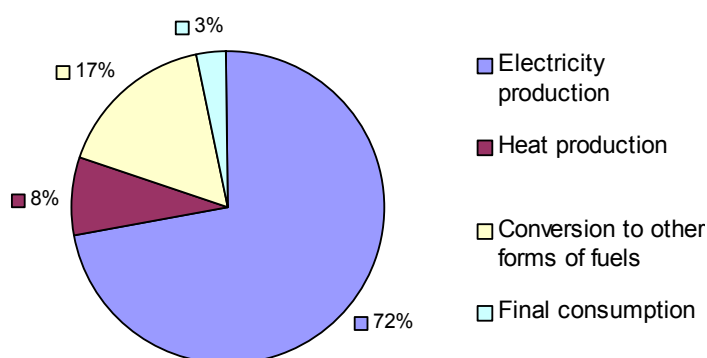


Figure 3. Average oil shale consumption by different activities (Gavrilova *et al.*, 2005).

About 19% of kukersite is used for retorting shale-oil and shale-gas (AS *Eesti Põlevkivi*, 2006). Three largest installations are at Eesti Power Plant (AS

Narva EJ Õlitehas), Kohtla-Järve (*Viru Keemia Grupp AS*) and Kiviõli (*Kiviõli Keemiatööstus*) (Figure 4).

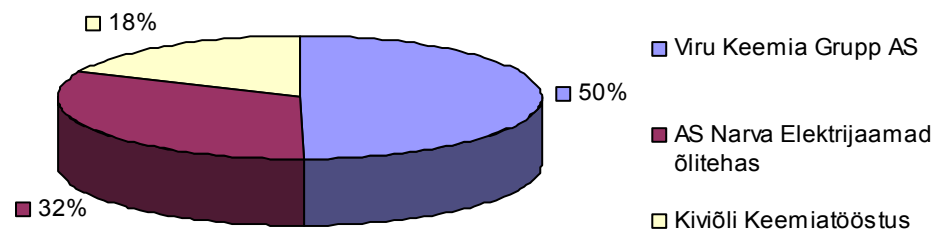


Figure 4. Respective share of enterprises in shale-oil production industry, at 2005 (*Viru Keemia Grupp AS*, *Kiviõli Keemiatööstuse OÜ*, *AS Narva Elektriijaamad*, 2006).

Oil shale retorting

Retorting is the process of heating shale to the temperature at which kerogen is decomposed or pyrolysed in the absence of oxygen into gas, condensable oil, and a solid residue. The inorganic mineral matrix of the shale is retained in the form of spent shale (Koel, 1999). Thermal destruction of kukersite begins at 170-180 °C and pyrogenous water appears at 270-290 °C. At the temperature 350-400 °C the organic substance of kukersite is converted into semi-liquid state, called thermobitumen (Kann *et al.*, 2004). The rate of kerogen (thermobitumen) decomposition is the highest at retort temperature of 480–520 °C on which the kerogen converts into three organic fractions: oil, gas and residual carbon. The gases and vapours leaving the retort are cooled to condense the oils and reaction water. Oil shale must pass the temperatures of thermobitumen formation and coking at a relatively high speed to avoid cracking and secondary pyrolysis of oil (Koel, 1999).

Over the past two decades, two main methods have been used in producing shale-oil: the “Galoter” process (or TSK process; old name UTT-3000), which has relatively higher energy efficiency than “Kiviter” process (see below) but it requires bulky and less reliable equipment. Kiviter process retorts with internal heating, but the energy efficiency is low and potentially hazardous semi-coke is formed as a by-product (Saether *et al.*, 2004).

The Kiviter vertical gas generator (GGG) (retort throughput 1000 t per day) is a vertical system internally heated by combustion of coke residue and non-condensable shale gas. Operation of the Kiviter retort is continuous. Raw shale enters from the top and is heated to temperatures required to decompose the organic matter. Heat is provided by the rising gases supplemented by recycle gas burned in the heat carrier preparation chamber. The combustion products pass sideward through the descending shale and carry the oil vapors and evolving gas with them into the collection chamber. From there they are delivered to the condensing system. Additional recycle gas and air are admitted to the chambers near 900 °C point and heat the shale residue to burn off the coke. Recycle gas (150-250 °C; Soone and

Doilov, 2003) enters the bottom of the retort and cools the spent shale, which then leaves the retort through a water-sealed discharge system (Koel, 1999). The Kiviter process was designed for the feed shale ranging from 25-125 mm (Soone and Doilov, 2003).

Kiviter process is suitable for retorting high-calorific (>11 MJ/kg) oil shales and oil yield is 15-17% from oil shale, production of gas is 380-430 m³ per tonne of oil shale, whereas the chemical efficiency of the process is 72-75%. The main drawbacks of the Kiviter process are:

- low energy efficiency;
- need of concentrated feed oil shale;
- direct burning of gas for heating up the heat carrier discharges vast volumes of low-calorific gas;
- due to incompletely retorted organic matter (up to 30% of organic matter gets lost with semi-coke; Veiderma, 2003) potentially hazardous solid retort residue (semi-coke) is formed as a by-product (Soone and Donilov, 2003).

The second type of retort is the Galoter retort (SHC, Solid Heat Carrier), which uses spent shale as a heat carrier. The process is based on introducing dried oil shale (< 2.5 cm particle size) into an aerofountain drier where it is mixed with hot (590-650 °C) shale ash produced by combustion of oil shale semi-coke (at 740-810 °C at oxygen deficiency) (Golubev, 2003). The oil yield of 11.5-13% in the Galoter process is 3-5% less compared to Kiviter process (Veiderma, 2003) but advantages of the Galoter process are:

- its solid residue is less harmful to environment, the concentration of organic substances is below 1%;
- unriched and lower calorific value oil shale is used;
- the chemical efficiency is up to 85% and the retort gas (40 m³ per tonne of oil shale) has high calorific value;
- high quality of products - fuel-grade shale-oil and raw materials for antiseptics, bitumen, mastics, adhesives etc.

The Galoter process has high retort throughput (an average of 3300 t per day) and is able to process technical rubber waste and petroleum washes as fuel (Golubev, 2003).

Since the Kiviter retort cannot accept fines below 25 mm and the Galoter retort requires fines smaller than 25 mm, then the two retorts complement each other for full resource utilization (Koel, 1999).

Dumping of spent oil shale (semi-coke) and its environmental impact

Total oil shale consumption for shale-oil production was 2.6 Mt in fiscal year 2004-2005. That makes 19% of all oil shale extracted annually (AS *Eesti Põlevkivi*, 2006). The mining and processing of 1000 Mt of oil shale in Estonia up to now has been accompanied with deposition of about 400 Mt of solid waste: total of 111.32 Mt of semi-coke deposited in heaps covering more than 200 ha, most of it is deposited at Kohtla-Järve (83.22 Mt, 74.7% of spent shale deposited). The next larger spent shale dumps are located Kiviõli and near the town of Narva with 19.2 Mt and 4.34 Mt respectively. Other minor locations Vanamõisa, Kohtla-Nõmme and Sillamäe hold 4.56 Mt of semi-coke combined (Veski, 2005).

Table 4. Volumes of spent shale in landfills formed in Estonian oil shale processing units 1921-2002, million tonnes (after Veski, 2005).

Location	Dry not reacted (1)	Used (2)	(1)-(2)	When reacted with H ₂ O	When reacted with CO ₂	With moisture (av.34.4%)	Share by locations, %
Kohtla-Järve	83.51	0.85	82.66	82.72	83.22	126.86	74.70
inc. chamber ovens	35.18	0.83	34.35	44.41	34.47	52.54	30.90
Kiviõli	18.59	0.02	18.57	18.65	19.20	29.27	17.20
Narva	4.08		4.08	4.13	4.34	6.61	3.9
Vanamõisa	2.51		2.51	2.51	2.77	4.22	2.5
Kohtla-Nõmme	0.91		0.91	0.91	1.09	1.66	1.0
Sillamäe	0.50		0.50	0.50	0.70	1.15	0.7
Total	110.1	0.87	109.23	109.44	111.32	169.77	100.0

Close to 300 Mt of combustion ashes have been generated up to now, about 263 Mt of which is accumulated in 1310 ha (settling ponds and the channel system around the ash heaps not included) of plateaus near the town of Narva (Narva Power Plants' ash plateaus) (Treatment plan..., 2006). All of these waste dumps are located in Ida-Viru County causing major environmental pollution sources in this region (Kahru & Põllumaa, 2006). About 80% of the total amount of waste generated in Estonia is generated in Ida-Viru County by the enterprises of oil shale processing and the hazardous oil shale related waste to total hazardous waste was 95% (Leevik *et al.*, 2004) (Table 5).

Table 5. The total amount of non-hazardous and hazardous waste generated in Estonia between 2000 and 2003 (after Leevik, *et al.*, 2004).

	2000, t	2000, t	2002, t	2003, t
Non-hazardous waste	5,650,099	6,632,752	7,998,566	10,856,031
...inc. rock heap	4,030,084	3,840,858	4,872,247	6,212,805
% from the total amount of non-hazardous waste	72%	58%	61%	57%
Hazardous waste	5,965,750	6,206,013	6,398,580	7,540,480
...including				
...semi-coke	1,007,047	1,107,895	810,925	815,714
...fuse	8,359	14,336	18,528	19,718
...oil shale bottom ash	4,780,417	4,776,582	5,157,871	2,654,046
...oil shale fly ash	149,191	140,862	184,162	3,679,572
% of waste from oil shale industry from the total amount of Hazardous waste	99.70%	97%	96%	95%

Oil shale semi-coke consists, in addition to mineral matrix, usually up to 10% of organics that may pose hazard to the environment due to leaching of toxic compounds as well as due to the self-ignition (Kahru & Põllumaa, 2006).

Chemical composition of semi-coke from Kohtla-Järve deposit (Table 6; Tang, 2003) is characterized by somewhat higher content of organic matter (9-16%) than indicated by Kahru & Põllumaa, (2004). The data also shows relatively high content of total sulfur that is concordant with the chemical composition of oil shales and low CO₂ content respect to CaO and MgO values.

However, chemical composition determined by Saether *et al.* (2004) suggests almost by an order of magnitude more Al₂O₃ and Fe₂O₃ and relatively higher amount of SiO₂ compared to Tang (2003). The amount of organics (C_{org}) in semi-coke on the other hand is considerably lower according to Saether *et al.*, (2004).

Table 6. Chemical composition of semi-coke from Kohtla-Järve semi-coke deposit (after Tang *et al.*, 2003).

	Retort 5	Retort 4	Old deposit	Slope (new deposit)	Washout plain
Composition of semi-coke, dry wt.% (105 °C)					
C _{org} (loss on ignition; 450 °C)	9.5	16.2	14.5	14	15.2
Mineral part (100 – organics)	90.5	83.8	85.5	86	84.8
Composition of semi-coke mineral matter, dry wt.%					
SiO ₂	25.0	21.6	21.2	18.8	21.8
Al ₂ O ₃	6.0	5.2	4.8	4.8	4.9
Fe ₂ O ₃	4.4	3.9	3.7	4.6	3.8
CaO	28.3	29.7	28.6	27.8	26.9
MgO	3.4	2.8	4.5	5.4	3.8
P ₂ O ₅	0.15	0.14	0.15	0.13	0.15
S _{total}	2.0	2.1	1.8	1.7	1.8
Na ₂ O	0.08	0.10	0.05	0.05	0.05
K ₂ O	2.5	2.2	1.8	1.7	2.2
TiO ₂	0.3	0.3	0.3	0.3	0.3
MnO	0.05	0.05	0.05	0.05	0.05
CO ₂	12.3	7.5	14.7	17.1	14.7
H ₂ O (hydroxide)	5.1	7.1	4.4	3.7	4.0
Total	89.5	82.7	86.1	85.9	84.4

Open deposition of semi-coke causes distribution of pollutants via air (dust) as well as via aqueous vectors (leaching by rainfall and snowmelt). Properties of spent shale vary widely with the retorting process but in general they contain significant amounts of total dissolved solids, sulfur compounds, carbonate, bicarbonate, and other inorganic ions, and lesser amounts of trace elements and organic compounds (Kahru & Pöllumaa, 2006). Also, thermal processing of oil shale and refining of the products of its semi-coking process (retorting) is accompanied with the formation of large amounts of different environmentally toxic process-waters and wastewaters containing phenols, tar and several other products. Water enters the technological process of oil shale thermal treatment from different sources:

- physical moisture in mined oil shale;
- water from oil shale semi-coking process (process water);
- precipitation in the factory's territory;
- leakages in cooling water system;
- used potable water and washwater, etc. (Kamenev *et al.*, 2003).

According to Kahru & Põllumaa (2006) oil shale combustion ashes and fresh semi-coke do not contain heavy metals, oil products, PAHs (polycyclic aromatic hydrocarbons) and phenols in hazardous levels but showed water-extracted toxicity, mostly due to high pH and probably also due to sulfides. However, semi-coke dump leachates contain 3-195 mg/l total phenols, including relatively stable 5-methylresorcinol and *p*-cresol, sulfuric compounds, PAHs, heavy metals and high alkalinity, which represent serious hazard to the environment, specifically the contamination of surroundings and waters in the region (Kahru & Põllumaa 2006). However, the environmental risk of leachates from the retort residue represent on ecosystem is not only related to the amount of potentially toxic trace elements in semi-coke. It also depends on the leachability of these elements in contact with water, leaching time, water throughput and elemental speciation (Saether *et al.*, 2004). Semi-coke heaps have been historically used for dumping of different wastes (fuses, waste sludge, sewage waters) that may explain the presence of phenols and other pollutants in the natural leachates and pore waters of semi-coke heaps. Old semi-coke dump leachates are practically neutral and considerably less toxic due to continuous rain washing. The decrease in toxicity of semi-coke during open deposition is probably a result of leaching of Ca and resulting decrease in alkalinity and probably also of evaporation (if volatile) or degradation of organic toxicants. The concentration of toxic compounds varies considerably in different semi-coke dumps. For example the Kiviõli semi-coke pore waters are by an order of magnitude less toxic than that of Kohtla-Järve (Kahru & Põllumaa, 2006).

Hydraulic discharge of solid waste after thermal treatment process is used in existing retorts and disposed in an open dump. In early years of shale retorting the waste was transported to the plateaus by horses, later a cableway with wagons was used. After discharging on top of the mountain, semi-coke was washed down with water. Today semi-coke is transported up with lorries and is laid onto the terrace at the foot of the “ridge”, (Pae *et al.*, 2005).

Material and methods

Studied semi-coke samples were collected at *Viru Keemia Grupp AS* semi-coke waste deposit plateau (Figure 5). Fresh semi-coke and waste plateau surface samples were collected by an author in October – November 2004. The samples of washout plateau deposits were obtained from six drillcores on the plateau by *IPT projektijuhtimine OÜ* in July 2004.



Figure 5. Studied fresh and hydrated semi-coke samples were collected from *Viru Keemia Grupp AS* semi-coke waste plateau in October – November 2004.

The mineralogical composition of semi-coke was determined by means of X-ray powder diffractometry (XRD). XRD analyses were carried out on:

- unhydrated (fresh) semi-coke;
- recently deposited semi-coke exposed for two weeks in atmospheric condition;
- drillcore samples (depth range 0.8-14.7 m) from the semi-coke waste heap and its foot areas (Figure 6).

Altogether 47 samples were investigated.

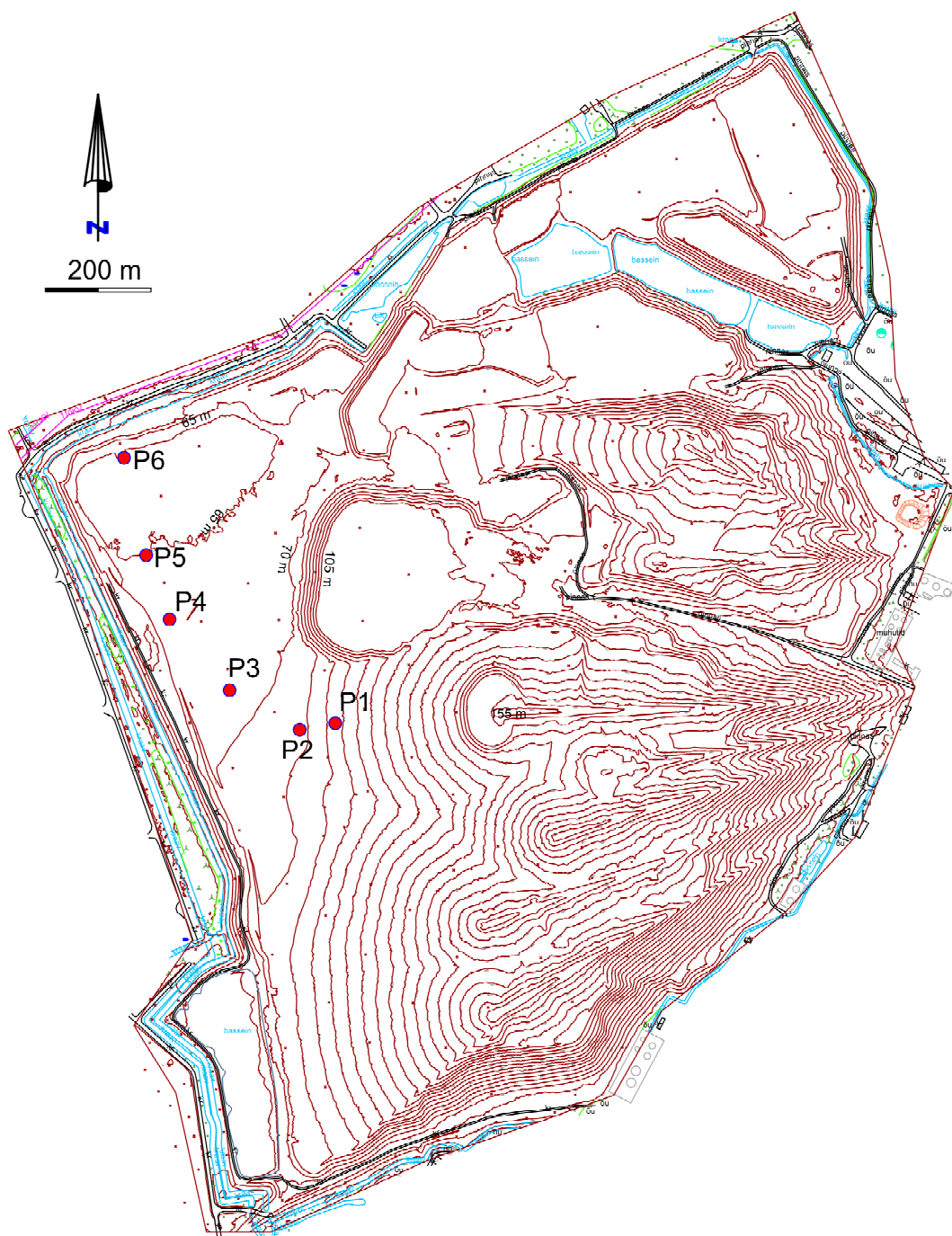


Figure 6. The scheme of the semi-coke waste mounds and plateaus at *Viru Keemia Grupp*, Kohtla Järve, and the location of studied drillcores P1 – P6 (Courtesy *Viru Keemia Grupp AS*, topography by *EOMap*, 2004).

To avoid additional hydration and carbonation all samples were analysed during 2-3 weeks after the sampling and the samples were stored airtight at refrigerator prior to analysis.

The mineralogical composition of studied samples was determined using Rietveld technique of X-ray diffraction analysis. Grinded and homogenized unoriented powder samples were prepared on Al-sample holders and exposed to CuK α radiation on Dron-3M diffractometer. Digitally registered diffractograms were measured at the interval between 2 – 50 °2 θ , with step 0.03 °2 θ and counting time 3-5 seconds. Quantitative mineral content was measured by Rietveld analyze based program SIROQUANT-2.5TM (Taylor, 1991). The full profile XRD pattern Rietveld method takes into account the integrated intensities of the particular diffractogram peaks and compares natural and artificial mixtures along the whole length of the diffractogram, providing thus considerably more information for mineral quantification (Ward *et al.*, 2001).

Operation of SIROQUANT involves interactive adjustment and best-fit matching of the XRD profiles for the individual minerals in the task file to the observed X-ray powder diffraction pattern. Overall intensities of the individual mineral phases, together with unit-cell dimensions, line-widths and preferred orientation for the minerals, and the zero setting of the diffractometer, were progressively refined under operator's instructions to obtain the maximum fit between the modeled and the full profile of the sample's XRD pattern. Weight percentages of different minerals and the errors for each mineral phase and the overall fit (chi² value) between the observed and computed profiles were calculated at each step.

Allowance was made in the SIROQUANT analysis for preferred orientation in several minerals, such as carbonates, whereas a match was obtained for the key peak positions, the distribution of peak heights was inconsistent with the standard mineral pattern. The standard patterns for such minerals were refined by SIROQUANT using computations based on the March-Dollase Function preferred orientation correction (Dollase, 1986) and the mineral

percentages adjusted accordingly (Ward *et al.*, 2001). The results of the SIROQUANT analysis represent the final output from each task when the best possible fit was achieved between the observed and calculated XRD patterns. The absolute error for each mineral phase is calculated according to the estimated standard deviation of each mineral quantity regard to Rietveld individual phase scale-factor (Taylor, 1991). An estimate of the overall quality of fit of each analyze is expressed as the relevant global χ^2 value. This should approach 1.0 for a perfect fit between the measured and interpreted patterns but in practice is usually greater than 1. χ^2 value less than 3 is considered “good”, less than 5 is “satisfactory”. For the present work χ^2 values between 2 and 4 were obtained.

For many of the minerals indicated by SIROQUANT to be present in low concentrations (<1%) the estimated error is of similar magnitude to, if not greater than, the actual determination. These minerals represent components for which small proportion or in some cases zero is indicated by the diffractogram but quantification is below the resolution of the Rietveld technique. In tabulations of the present work these minerals are shown as traces (marked in table as tr.) and they are not taken into account when the remaining components were normalized to 100%.

Micromorphology and spatial relationships of secondary mineralization were carried out using scanning electron microscope (SEM) *Zeiss DSM 940*. SEM preparations were coated with conductive gold coating during preparation.

To minimize any hydration and oxidation effects on fresh semi-coke all of the samples were frozen instantly in liquid nitrogen and sublimated in vacuum drier prior to analyses. XRD preparations made from samples were measured within 4 hours after the preparation was made. The waste plateau samples were dried at 105 °C for 24 h prior to XRD preparation.

Results

The mineral composition and representative XRD patterns of studied samples is shown in tables 7, 8 and figures 7, 8 and 9.

XRD mineralogy

Fresh semi-coke

The predominant phases identified by X-ray diffraction in a fresh unhydrated semi-coke (Table 7, Figure 7) were calcite, dolomite, quartz, K-feldspar and clay minerals (mostly illite), which are typical constituents of oil shale mineral matter and were preserved or slightly changed during the retorting process. However, the composition of semi-coke clearly indicates the decomposition of dolomite respect to average oil shale (Figure 8a). In addition to these minerals, fresh semi-coke contains secondary phases formed by partial thermal decomposition and subsequent reactions of carbonate and clay minerals – melilite $[(Ca,Na)_2(Al,Mg,Fe)(Si,Al)_2O_7]$, periclase $[MgO]$, clinker-minerals: bellite $[\beta-C_2S]$, merwinite $[Ca_3Mg(SiO_4)_2]$. Also oldhamite $[CaS]$ together with traces of FeS – mackinawite were identified in fresh semi-coke.

Table 7. Average mineral composition of fresh semi-coke and the same material hydrated sampled after two weeks of hydration under ambient conditions, wt%; tr. – *traces*.

Material	Quartz	K-feldspar	Albite	Illite+Smeectite	Bellite (β -C2S)	Merwinite	C3A	Periclase	Melilite	Calcite	Dolomite	Oldhamite	FeS (Macinawite)	Ettringite
Fresh	13.6	18.6	tr.	15.3	5.4	2.8	tr.	2.0	9.5	25.5	4.3	3.0	tr.	
Hydrated	11.4	11.2	tr.	14.3	6.6	4.0	tr.	1.5	5.4	29.3	3.1			13.2

Studied samples do not contain in measurable amounts (detection limit 1%) of minerals common to thermally treated limestone like lime $[CaO]$ or its hydration product portlandite $[Ca(OH)_2]$ nor anhydrite $[CaSO_4]$, which are typical phases in oil shale combustion ashes (e.g. Kuusik *et al.*, 2005). XRD

analyse is unable to identify the amorphous phase (non-crystallised matter). However the diffuse maximum from amorphous phase scattering in measured XRD diffractogram indicates the quantity of non-crystallised matter to be as high as 10(20)%.

Fresh semi-coke contains occasionally yellowish-green lumps of partially melted slag, which are composed of high-temperature Ca-Mg silicates – diposide, enstatite and various clinker-minerals (β -C₂S, C₃S, merwinite and traces of Ca-ferrites).

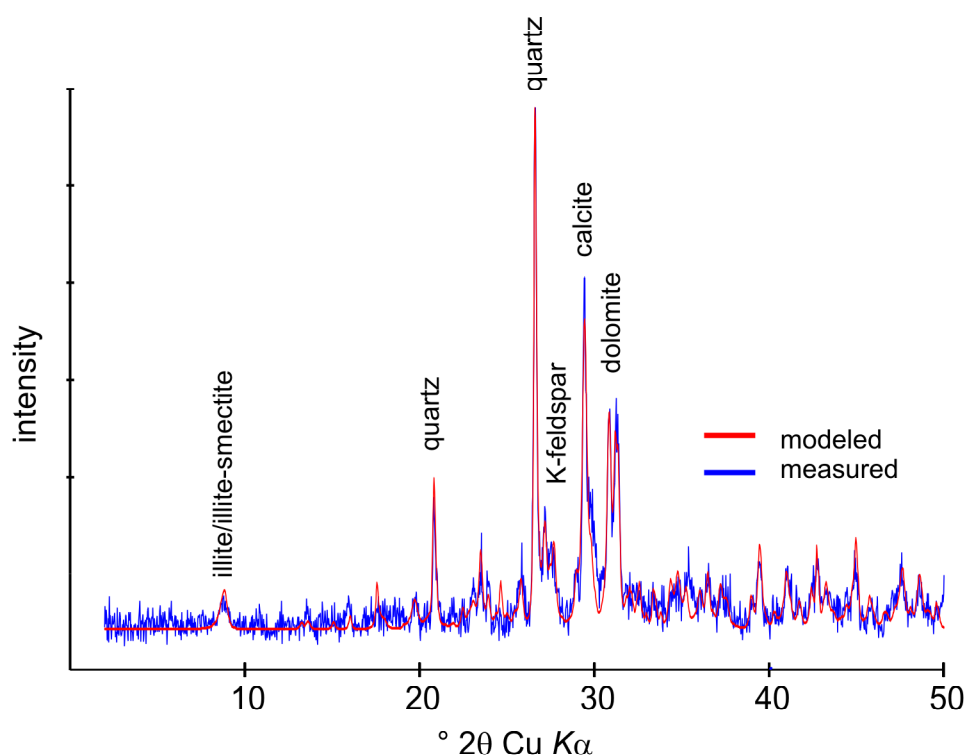


Figure 7. Representative XRD pattern of fresh unhydrated semi-coke.

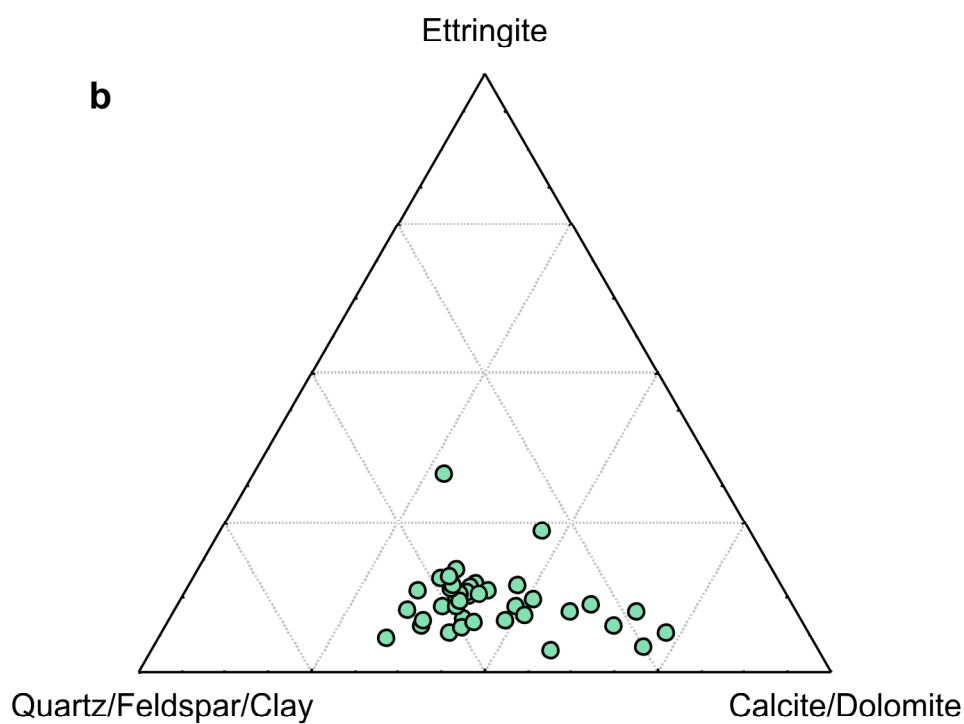
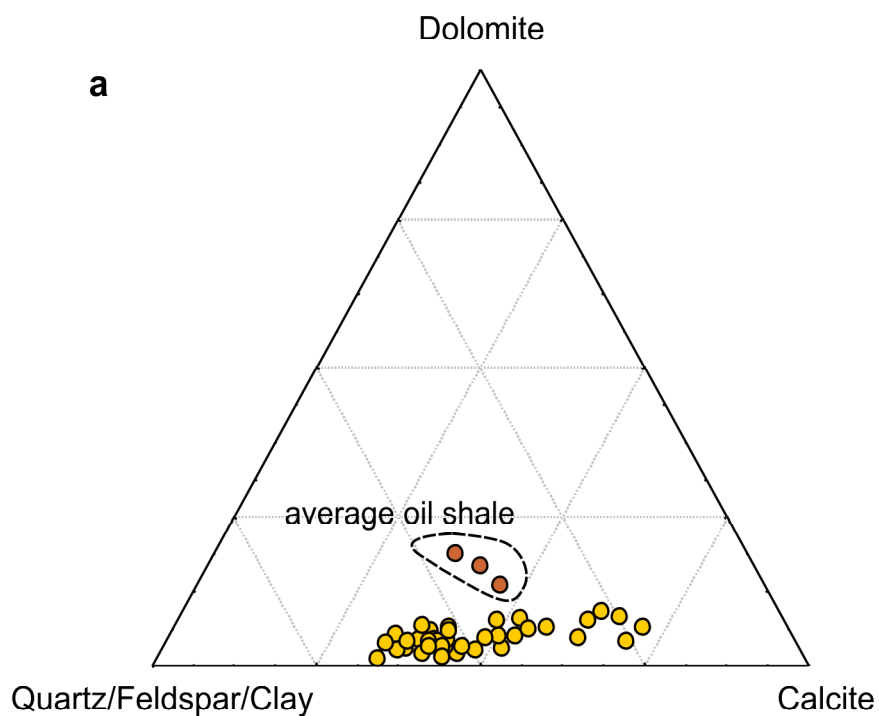


Figure 8. Mineralogical composition of semi-coke samples, (a) – semi-coke composition compared to average oil shale (oil shale composition – unpublished data by K. Kirsimäe, 2006), (b) – terrigenous, carbonate and authigenic phases of semi-coke.

Hydrated semi-coke and plateau deposits

The most notable difference between the fresh and deposited semi-coke is the disappearance of oldhamite [CaS] and the occurrence of considerable amount of ettringite [$\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12}\cdot 26\text{H}_2\text{O}$] (Table 7, Figures 8b, 9). The average abundance of minerals fluctuate for some amount, which is probably due to the variations in the original deposited matter and its' later alteration.

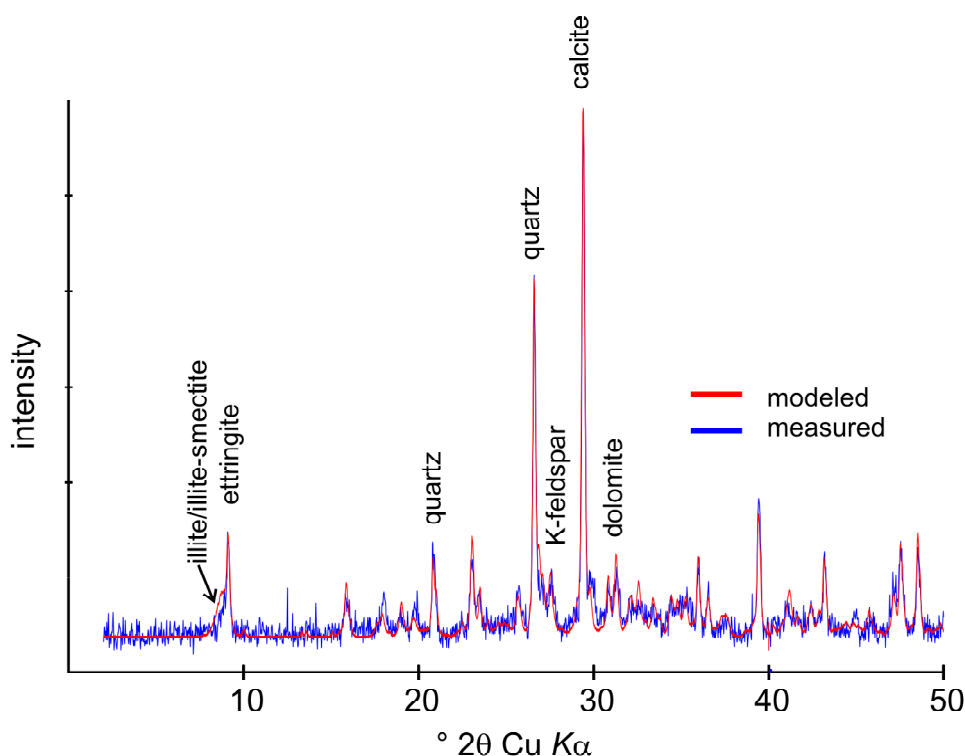


Figure 9. XRD pattern of hydrated semi-coke. Note the appearance of ettringite.

Mineralogical composition of semi-coke matter in washout plateau samples is rather uniform. However, there are certain variations evident in drillcore samples from various locations and depths. The dominant phases in all drillcore samples P1-P6 are calcite and dolomite; quartz, feldspars (K-feldspar and in trace amounts of albite), clay minerals (Illite/illite-smectite); and ettringite (Figure 9, Table 8). The content of the rest of the minerals present in studied samples (different clinker-minerals) are usually below 5%.

The studied drillcores (P1 to P6) are aligned along a profile that reveals sediments from the foot of the waste mound to washout plateau. Section

variation, where carbonate minerals, both calcite and dolomite content is highest is in P1, up to 61.2% and 11.2% respectively (average values of 49% and 5.9% respectively), whereas the amount of terrigenous minerals is consequently lower – on average of 8.4% quartz; 6.6% feldspars and 13% clay minerals (Table 8, Figure 10).

Ettringite shows considerable variation from 3.5% to 20.3%, with an average of 9%. The content of gypsum and other minor minerals like periclase and hydrocalumite is around 1% or slightly less. The variation of clinker-minerals bellite and merwinite is notable, but as their overall content is less than 5% (only occasionally as high as 4.6% of bellite) its' variation significance is low. Slag mineral melilite was also detected in all samples varying from 1.1% to 5%.

The same relationship between mineral content can be applied to samples from drillcore P2. The most notable difference is the reduction in carbonate content, an average of 35% calcite and 3.7% dolomite. The amount of terrigenous minerals (13.6% quartz and 9.8% feldspars) respect to carbonates are much higher compared to P1, especially the quantity of clay minerals with an average of 20.9%. Ettringite content has risen slightly compared to P1 (10.7%).

In drillcore P3, there is further increase in contents of quartz and feldspars, thou the increase is minor (15.3% and 11.4% respectively). The relative share of clay minerals among dominant phases (avg. 17.1%) is smaller than in P2 and its content variation is considerably lower. The content of rest of the mineral phases present is approximately the same as in P2 with few exceptions:

- twofold increase of bellite average value (4.5%);
- a disappearance of gypsum, which may be due to the limited detection capacity of XRD method of low content constituents;
- an appearance of 2.3% jarosite $[\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6]$ in the uppermost sample.

Table 8. Mineralogical composition of semi-coke samples, weight

Lab. no	Sample / Drillcore	Depth, m	Quartz	K-feldspar / Albite	Illite/ Illite-Smectite	Calcite	Dolomite	Etringite	Beilite(C2S)	Melilitite	Hydrocalumite	Merrinitite	Gypsum	Jarosite	Periclase
E 27	P1 0.8-1.0	0.9	5.9%	7.9%	11.3%	52.0%	6.7%	7.2%	3.1%	2.0%			0.9%		1.00%
E 34	P1 2.7-3	2.85	14.1%	8.3%	13.7%	46.4%	7.3%	3.5%	2.1%	3.3%					
E 28	P1 4.7-4.9	4.8	8.4%	5.3%	9.3%	53.7%	11.2%	4.0%	2.3%	1.1%			0.8%		
E 25	P1 7.2-7.4	7.3	3.8%	4.5%	10.7%	61.2%	5.8%	6.1%	2.3%	2.6%	0.80%				
E 26	P1 8.8-8.9	8.85	5.7%	4.9%	11.4%	59.6%	3.8%	9.7%	2.1%	2.8%	0.80%	2.40%			
E 22	P1 10.8-11.0	10.9	6.4%	8.0%	11.4%	35.2%	4.3%	20.3%	4.6%	5.0%			1.4%		
E 24	P1 12.5-12.7	12.6	7.7%	6.5%	16.4%	47.2%	5.7%	9.4%	1.5%	4.8%			1.1%		
E 23	P1 14.5-14.7	14.6	15.0%	9.4%	19.9%	37.0%	2.3%	12.2%	tr	3.4%	1.80%				
E 55	P2 1.2	1.2	15.2%	11.5%	9.3%	41.0%	2.5%	10.1%	4.8%	2.8%	0.70%				
E 48	P2 1.5-1.7	1.6	11.2%	7.8%	18.4%	41.4%	6.7%	9.2%	1.2%	3.3%	0.70%	1.60%			0.60%
E 53	P2 3.6-3.7	3.65	15.6%	9.4%	21.1%	32.8%	5.3%	11.3%		2.7%	0.60%	0.90%	1.8%		
E 51	P2 5.2-5.4	5.3	9.8%	11.3%	21.2%	34.0%	5.5%	14.3%		3.8%					
E 54	P2 6.6-6.8	6.7	10.4%	9.1%	20.5%	38.3%	2.4%	13.0%	0.9%	3.9%			1.6%		
E 50	P2 8.2-8.3	8.25	13.0%	10.0%	25.2%	32.1%	4.0%	10.6%		3.9%			1.1%		
E 49	P2 9.9-10.0	9.95	19.4%	10.9%	29.1%	30.4%	1.3%	5.7%		2.4%	1.50%				
E 52	P2 11.6-11.8	11.7	15.0%	10.1%	22.4%	37.0%	4.0%	8.9%		2.6%					
E 56	P2 13.4-13.6	13.5	12.8%	7.9%	20.9%	28.6%	1.8%	13.4%	2.9%	3.1%	0.50%	1.50%	1.5%	2.30%	1.00%
E 16	P3 1.5-1.6	1.55	21.0%	12.9%	15.9%	28.3%	4.5%	7.2%	4.6%	2.4%	0.60%	0.80%	tr?		
E 17	P3 3.4-3.5	3.45	14.3%	13.7%	19.0%	34.0%	3.6%	6.0%	5.3%	4.2%	1.70%	2.10%			
E 18	P3 5.1-5.3	5.2	18.3%	10.2%	17.4%	33.8%	3.9%	10.6%	3.2%	2.7%	1.60%	2.90%			
E 19	P3 7.2-7.3	7.25	13.8%	10.1%	16.5%	34.5%	1.8%	12.8%	4.7%	3.8%	0.70%	1.40%			
E 20	P3 8.4-8.5	8.45	12.4%	12.2%	20.0%	35.3%	3.0%	6.7%	5.9%	4.4%	1.10%				
E 21	P3 9.9-10.0	9.95	12.1%	9.1%	14.0%	39.2%	4.2%	13.6%	3.4%	4.4%					
E 45	P4 1.4-1.5	1.45	11.2%	10.5%	16.8%	39.3%	4.1%	8.0%	4.9%	3.8%					
E 42	P4 3.2-3.3	3.25	16.3%	9.3%	17.9%	34.0%	1.8%	11.7%	3.9%	2.8%			1.0%		
E 43	P4 5.1-5.2	5.15	15.2%	10.0%	17.0%	33.6%	3.7%	12.4%	2.0%	3.1%	1.30%		1.6%		
E 46	P4 5.7-6.8	6.2	12.7%	10.4%	17.2%	35.6%	2.8%	12.0%	3.0%	5.1%	1.40%				
E 47	P4 8.3-8.4	8.35	15.0%	7.5%	23.3%	37.0%	5.4%	8.1%	0.5%	2.2%	1.00%				
E 44	P4 9.8-10.0	9.9	15.2%	10.2%	18.0%	32.7%	3.6%	12.1%	1.2%	4.3%	1.50%		1.6%		
E 36	P5 1.3-1.5	1.4	13.6%	10.4%	17.6%	32.2%	2.6%	10.5%	3.8%	4.7%	1.20%				
E 35	P5 2.2-2.3	2.25	16.1%	11.7%	21.5%	30.1%	2.7%	7.8%	3.5%	2.8%					
E 39	P5 5.0-5.2	5.1	17.6%	12.2%	18.7%	28.1%	2.4%	12.5%	2.8%	3.7%	0.90%		2.0%		
E 38	P5 6.8-6.9	6.85	14.9%	8.6%	10.0%	41.5%	4.3%	11.0%	5.7%	2.9%	0.70%				
E 32	P5 8.4-8.5	8.45	11.5%	11.1%	18.2%	31.7%	1.3%	15.3%	3.2%	4.6%	0.80%		1.6%		
E 37	P5 9.8-10.0	9.9	14.8%	10.7%	18.0%	31.0%	3.5%	12.6%	3.3%	3.9%					
E 29	P6 1.1-1.2	1.15	8.0%	5.9%	11.4%	47.7%	3.8%	10.0%	8.4%	5.3%					
E 30	P6 2.9-3.0	2.95	16.6%	10.3%	16.6%	29.2%	5.4%	13.4%	4.3%	4.4%					
E 40	P6 6.1-6.3	6.2	13.1%	13.7%	15.6%	30.3%	2.7%	14.6%	4.5%	4.6%			1.0%		
E 41	P6 8.1-8.2	8.15	17.5%	13.7%	20.8%	27.5%	3.5%	9.8%	2.5%	3.7%	1.20%	1.60%	0.9%		
E 31	P6 9.8-10.0	9.9	14.9%	10.0%	12.0%	22.7%	2.8%	31.2%	2.7%	3.7%	1.10%		tr.		

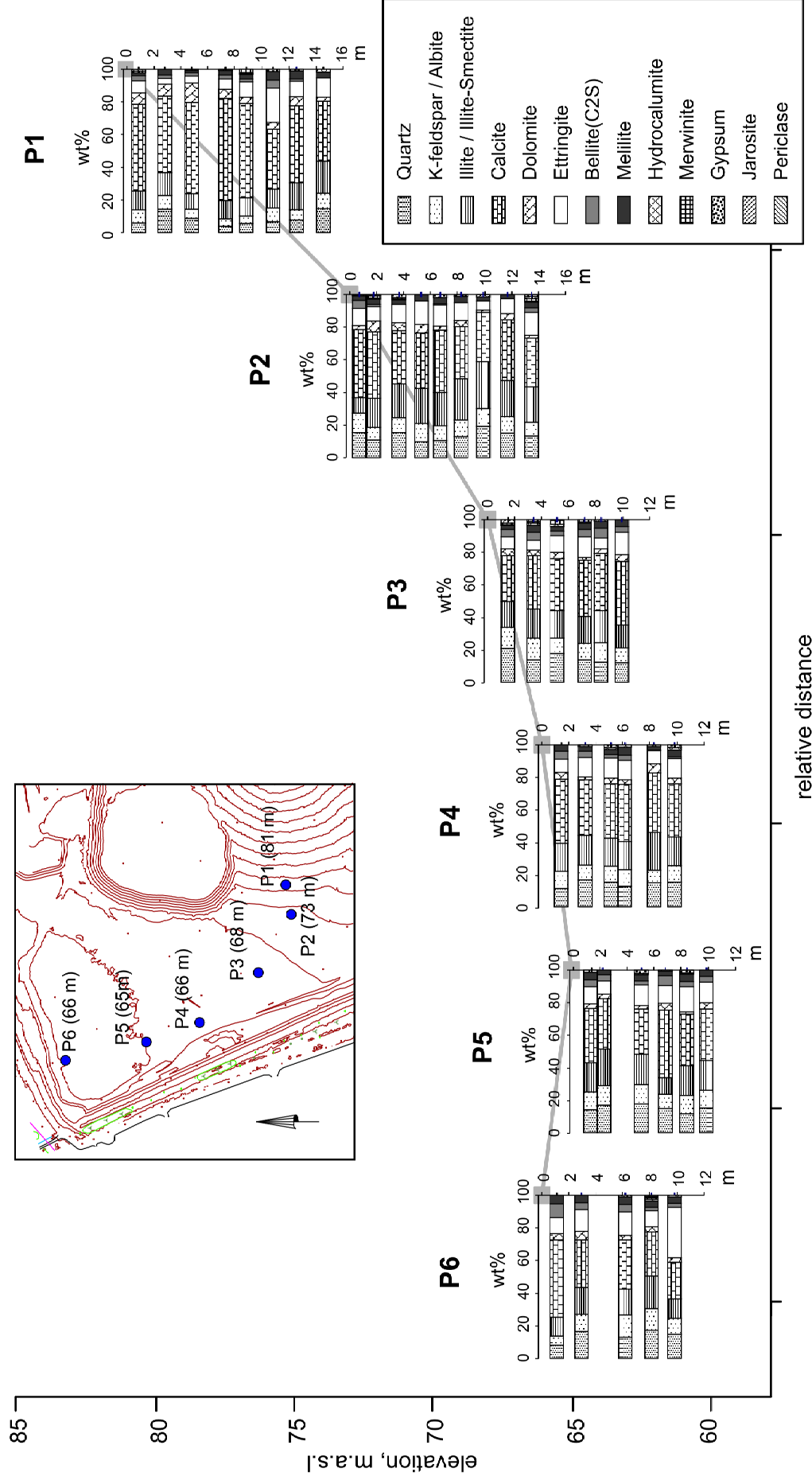


Figure 10. Mineralogical composition of studied samples along the relative profile on the semi-coke waste plateau. Inset shows the location of drillcores along the profile.

The composition of sediments in P4 and P5 compared to P3 is principally the same. The individual phase variations of mineralogical composition within the range of drillcore material (e.g. quartz and feldspars) tend to be smaller than in P1-P3.

Illite/illite-smectite and calcite deteriorate somewhat from that trend in P5. Only the ettringite content has slightly increased (avg. 10.7% and 11.45% in P4 and P5 respectively) (Figure 10). Also, the sediments in drillcore P6 are similar to previous (P5), but calcite content (31.4%) is the lowest value for calcite found in all studied drillcore samples. However, the quantity of ettringite is the highest, with the maximum value of 31.2% (avg. 15.3%). Bellite and melilite also display higher values, an average of 4.5% both.

The first two drillcore samples P1 and P2 are collected from the lower part of the slope (P1) and from the foot (P2) of the semi-coke heap. Samples from those two locations show decreasing trend of calcite and dolomite content with growing depth and the opposite trend is characteristic of clay minerals. Also the extent of variation of mineral phases within the range of drillcore samples is relatively extensive especially in the first drillcore location (P1).

Sediments in drillcores P3 – P6, on the other hand, are collected from the washout plain, which has been formed by the finer fraction washed out from the semi-coke material deposited on the waste mounds and transported down onto the plateau mostly by water used during waste “washdown” and by rainwater. Sediments from P3, P4 and P5 lack these relatively distinct trends between the depth and the increase of content variation among the dominant phases.

At the same time the content variation of individual phases in washout plateau sediments is smaller than on the foot of the mound. Exception from these trends is sediments in most distant drillcore P6, which is similar to the sections observed in P1 and P2 that are characterized by increase of clay mineral content and decrease in carbonates along the depth vector. Such

trends relation to depth vector for minor phases (bellite, gypsum, melilite etc.) are indistinct or absent.

Particularly interesting feature among all studied samples is a slight increase in ettringite content with increasing depth. However, the increase is not expressed very clearly and the content variation is considerable (Figure 11). Also, there is a small, but consistent increase of ettringite along the profile from the uppermost drillcore P1 to the lowermost cores P5 and P6 (Figure 12).

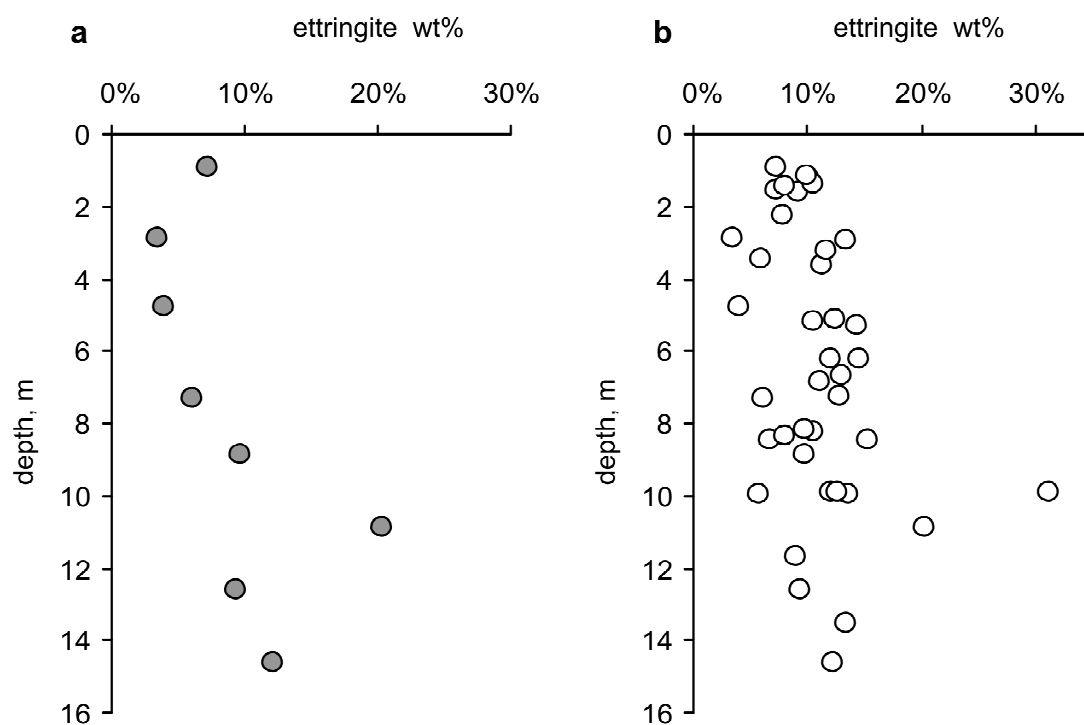


Figure 11. Ettringite content variation with the depth. (a) – drillcore P1 and (b) – all studied drillcore samples.

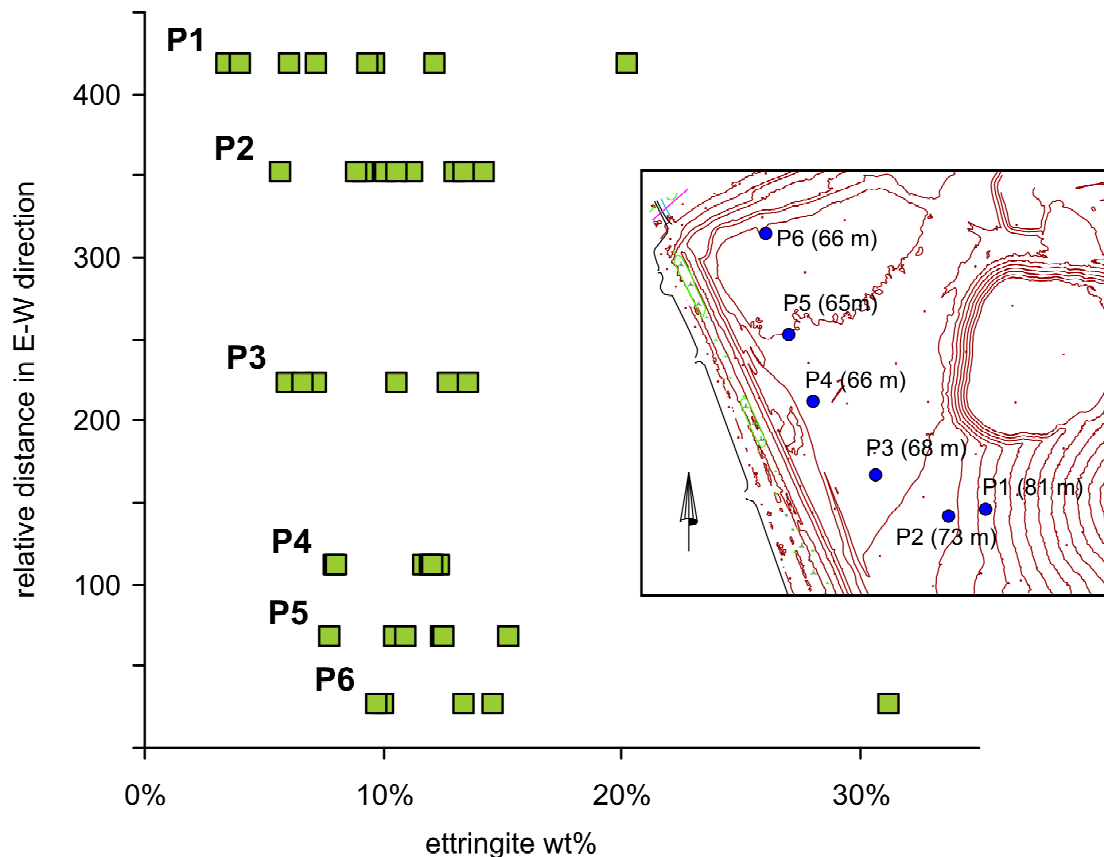


Figure 12. Ettringite content along the P1- P6 drillcore profile. The inset shows the location and height of the drillcores.

Scanning electron microscopy

Scanning electron microscopy (SEM) studies were undertaken primarily to study the occurrence and spatial distribution of ettringite as a major secondary phase.

SEM micrographs of unhydrated semi-coke show very porous material, composed of different sized particles (Figure 13a). Secondary ettringite forms 2-10 μm long prismatic crystals that precipitate and form irregular aggregates in semi-coke open pores (Figure 13b,c,d) or develop as spherulitic aggregates of radially oriented crystallites on fracture planes (Figure 13e). In P5 drillcore samples ettringite crystals show signs of partial dissolution (Figure 13f).

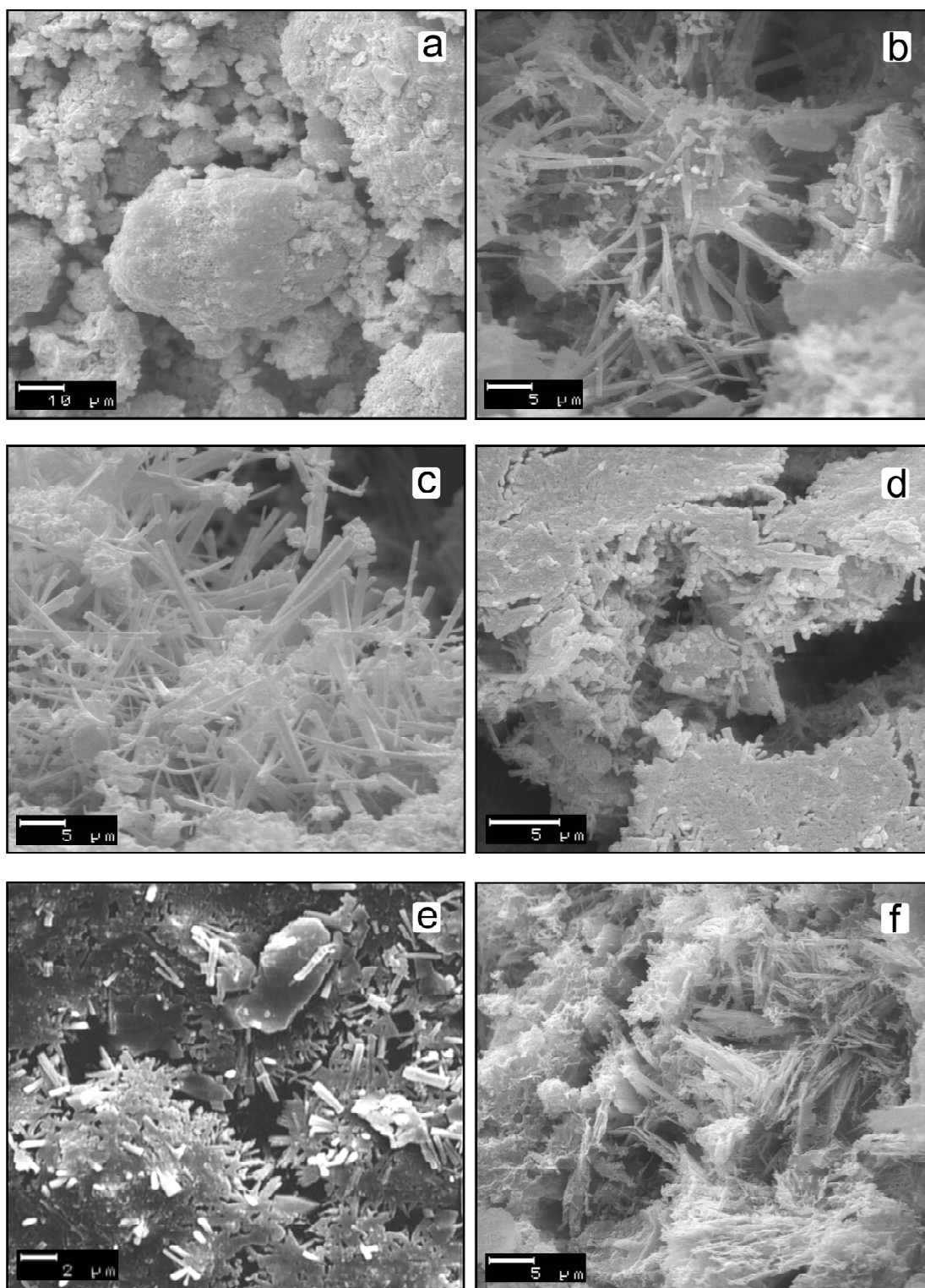


Figure 13. SEM micrographs of semi-coke samples. (a) – fresh, unhydrated sample. In semi-coke pores ettringite forms irregular prismatic (b,c,d) and/or spherulitic aggregates of radially oriented crystallites on fracture planes (e); (f) – a micrograph of partially dissolved ettringite crystals

Discussion

Mineral transformation in thermal decomposition/processing of oil shale

The solid retort residue in Kiviter process – the semi-coke is formed by the transformation of oil shale as a result of its partial thermal decomposition in two stages:

- (1) semi-coking process at temperatures of 400-520 °C, and
- (2) short heating at 900-1000 °C during the final stage of retorting, which is used to burn off the coke residue.

Semi-coke itself is a complex mixture, which contains alongside with transformed matter also pieces of macroscopically unaltered oil shale that shows only slight signs of thermal decomposition, and lumps and pieces of partly altered carbonate rock together with lumps of partially melted slag.

The changes of mineral matter during the first stage of the retorting process, which occurs at air deficiency conditions, are negligible. Terrigenous fractions of the oil shale – quartz and feldspars – remain practically unchanged and only clay minerals start to dehydrate. At temperatures 500 °C and above the kaolinite decomposes to metakaolinite- and mullite-type aluminosilicate mass. However, the kaolinite content in oil shale respect to overall oil shale mineral composition is less than 5% and this transformation has no determinative importance. Nevertheless, at these temperatures (~400-500 °C) various sulfur compounds (mainly in the form of pyrite and/or marcasite - FeS_2) start to decompose. The sulfur released by pyrite decomposition and the free CaO released from partial pyrolysis of calcium carbonate are reacting by forming CaS type phases, whereas the uncompleted decomposition process of pyrite may produce mackinawite $[\text{FeS}]$ type phases.

At the final step of retorting the temperatures of 900-1000 °C are applied to burn off the organic matter/coke in solid residue. In this process a slag-like material forms, which consists of:

- amorphous phase at the expense of the decomposition and melting of aluminosilicate minerals (clays);
- Ca-silicates – melilite, cement minerals like belite [β -C₂S], merwinite, etc., that form in reactions between free Ca and Mg oxides derived from the decomposition of dolomite (decomposition starts at ~860 °C) and calcite (decomposition at ~950 °C), and aluminosilicates (mainly clay minerals and K-feldspar) and less quartz.

Moreover, mineral composition of slag lumps found in semi-coke indicates that temperatures as high as 1400-1500 °C can occur locally during this stage.

Hydration and diagenesis of semi-coke sediments

Many of the mineral phases formed in oil shale retorting/semi-coking process are unstable in atmospheric conditions. Deposition of spent shale on waste dumps initiates the mineral transformation, predominantly hydration and carbonation. The dominant hydration product of semi-coke is secondary ettringite – $\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12}\cdot 26\text{H}_2\text{O}$. The formation of ettringite occurs as a result of the reaction between CaO, formed at thermal decomposition of limestone/dolomite, with Al-compounds derived from the partial decomposition of clay minerals and/or feldspars, and with the dissolved sulfur compounds and/or CaS (oldhamite), emitted in the combustion process of organic matter or decomposition product of pyrite and carbonate phases, respectively.

The precipitation kinetics of ettringite is rapid. In laboratory experiments (Myneni *et al.*, 1998) the nucleation of ettringite crystallites is fast and the white ettringite precipitate appears immediately after mixing of CaO and $\text{Al}_2(\text{SO}_4)_3$ solutions. However, ettringite formation in semi-coke deposits under atmospheric conditions is much slower and the ettringite formation occurs over two-three weeks. Although nucleation can be assumed to begin in matter of hours, the crystalline ettringite appearance takes days or weeks. Controlling factors of ettringite precipitation are dissolved Ca^{2+} , Al^{3+} and SO_4^{4-}

ion concentrations and their activities, which depend on ionic strength of the semi-coke pore-water. Unlike to oil shale combustion ash plateau sediments, where the most probable inhibiting factor of ettringite formation is sulfate deficiency (Puura, 1992), thou in semi-coke deposits the controlling agent seems to be the availability of CaO and/or Ca(OH)_2 that are readily susceptible to chemical reactions. In semi-coke sediment it is probable that at the presence of high sulfate activity all of the free Ca will be bound to form ettringite.

Crucial factor for the formation and stability of ettringite is pH. In alkali and sulfate-rich solutions ettringite is the most stable phase of Ca(OH)_2 – $\text{Al}_2(\text{SO}_4)_3$ – H_2O system. Ettringite is stable at pH values >10.7 , in lower pH values ettringite dissolves incongruently to gypsum, (amorphous) Al-hydroxide and Ca-aluminate type phases (Myneni *et al.*, 1998). At high pH values one of the solubility products is portlandite (Figure 14) (Jones, 1944 cit. Myneni *et al.*, 1998). However, at high CO_2 partial pressure and relatively low pH level, ettringite decomposes into sulfates and aragonite [CaCO_3] with vaterite [γ - CaCO_3] as an intermediate phase (Nishikawa *et al.*, 1992). Moreover, decomposition of ettringite (decomposition rate) is also influenced by temperature and the content of different compounds found in deposit. At high temperatures monosulfoaluminate [$\text{Ca}_4\text{Al}_2(\text{SO}_4)(\text{OH})_{12}\cdot 6\text{H}_2\text{O}$] phase is stable over ettringite, whereas according to Pajares *et al.*, (2003) ettringite solubility is inhibited on the presence of CaCO_3 (calcite) and cement clinker-minerals: bellite [C2S], alite [C3S] etc. Those phases have the capacity to buffer solution pH to the critical levels for ettringite stability.

When the Ca(OH)_2 – $\text{Al}_2(\text{SO}_4)_3$ – H_2O system is open to atmospheric CO_2 , then its solution approach the saturation of carbonate mineral phases such as calcite and aragonite under alkaline pH conditions. However, the slow precipitation kinetics of calcite associated with the slow transport of CO_2 into the waste materials delays its formation relative to ettringite and gypsum. Moreover, high SO_2^{4-} activity favors the formation of gypsum over calcite (Doner and Lynn, 1989). This has also been observed from field studies of ettringite-bearing, weathered, flue-gas desulfurization (FGD) materials. In

these alkaline materials calcite did not appear until 240 days of weathering (Doner and Lynn, 1989). However, elevated CO_2 partial pressures from the decomposition of organic matter in subsurface soil horizons or prolonged leaching of SO_4^{4-} from waste materials should favor the calcite formation.

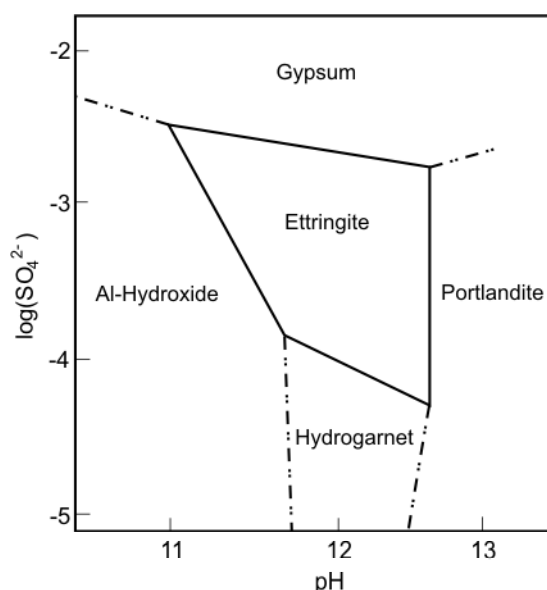


Figure 14. Ettringite stability in alkaline environments (after Hampson and Bailey, 1982 cit Myneni *et al.*, 1998)

It is important to note that in semi-coke deposits ettringite acts as a cement mineral and by binding waste particles forms monolithic deposit, therefore stabilizing semi-coke dumps geotechnically. It has also been shown that ettringite formation controls the activity of several contaminants, both cations and oxoanions and is concomitant with the reduction of leachate trace elements (Fowler *et al.*, 1993).

Most prominent difference of the semi-coke compared to oil shale combustion ash deposits (e.g. Kespre, 2004) is the absence of portlandite $[\text{Ca}(\text{OH})_2]$ and hydrocalumite $[\text{Ca}_2\text{Al}(\text{OH})_7 \cdot 3\text{H}_2\text{O}]$ – common constituents in ash sediments. However, high pH (12-13) of semi-coke leachates suggests the presence of some amount of portlandite in semi-coke, but its quantity remains probably below 1% that is under the detection limit of X-ray diffraction analyses. The

presence of small amount of portlandite (~0.6%) in semi-coke was confirmed by titration experiment where semi-coke leachate pH was measured at different sediment–water ratios. The pH value in oversaturated solution respect to portlandite is 12.4 at 25°C and the portlandite content in semi-coke matter was found from saturation – undersaturation equilibrium.

The restricted occurrence of portlandite would suggest also limited carbonation of the semi-coke sediments. However, the SEM studies show the presence of authigenic calcite aggregates in semi-coke sediments. Preconditions for carbonation process are dissolution of ettringite and the reaction with atmospheric carbon dioxide (CO₂) to form significantly stronger and less soluble calcium carbonate phase calcite, aragonite or possibly vaterite (γ-CaCO₃). For carbonation to occur, the presence of water is essential, since it requires the dissolution of CO₂.

The inner structure of semi-coke deposits exhibits considerable variation, which is probably due to both physical and chemical separation during deposition of the sediment and due to different diagenetic/hydration processes. The surface layers of the semi-coke plateau and the “mountain” are under constant influence of percolating precipitation water, which considerably lowers the pH of porewater in the upper layers and thus initiates in the first place the dissolution of ettringite. The studied sections indicate that, although not well expressed in all sequences, the ettringite dissolution profile can be traced to several meters depth.

The remarkably higher content of calcite and dolomite in samples from drillcore P1 is probably location specific. The site is located on the foot of the semi-coke waste heap (Figure 6), whereas the rest of the drillcores were drilled on the semi-coke washout plateau. Elevated content of carbonates and respectively lower amount of terrigenous material (specifically clays) in P1 can be linked to development of more intensively leached profiles on the top and slopes of waste heaps, which are similar to leached soil profiles where fine grained clay minerals are systematically transported down the slope by

percolating waters. However, the most feasible explanation is the gravitational separation during the dumping of the material. The material deposited in studied area of the waste plateau was dumped in large mounds. By dumping, the waste material fractionates gravitationally with largest particles transported onto the foot area of the mound (Puura & Pihlak, 1998). The largest particles in semi-coke are usually partially decomposed harder lumps of oil shale and especially carbonate rocks, which is also reflected in the mineral composition of the sediment.

Summary and conclusions

The first systematic mineralogical study of the semi-coke and its sediments shows that:

The predominant phases in a fresh unhydrated semi-coke are calcite, dolomite, quartz, K-feldspar and clay minerals (mostly illite). Also, phases like melilite, periclase, bellite, merwinite, formed by the partial thermal decomposition and subsequent reactions of initial minerals. Importantly the CaS phase oldhamite together with traces of FeS mineral mackinawite were identified in fresh semi-coke. The composition of semi-coke reflects the changes of mineral matter during the retorting process. During the main phase of retorting at temperatures ~400-520 °C only dehydration and partial transformation of clay minerals as well as the decomposition of sulfur compounds (pyrite, marcasite) occur. At the final step of retorting during short heating to temperatures 900-1000 °C a slag-like material forms which consists of amorphous and Ca-silicate phases.

During the deposition and hydration the composition of semi-coke changes and unstable phases (e.g. oldhamite) disappear and is replaced by considerable amount of Ca-Al-sulfate – ettringite. Controlling factors of ettringite precipitation and stability are dissolved Ca^{2+} , Al^{3+} and SO_4^{4-} ions from dissolution of unstable thermal decomposition products. Important parameter for ettringite formation and stability is pH as ettringite is stable at pH >10.7 below that ettringite dissolves incongruently to gypsum, (amorphous) Al-hydroxide and Ca-aluminate type phases.

The composition of mineral matter in oil shale retort waste heap is relatively uniform. The most notable changes in studied drillcore sections as well as along the P1 – P6 profile are the decrease in carbonate content and increase in clay mineral content. Also, ettringite content increases slightly in the whole range of drillcore sampling points both vertically and horizontally.

The inner structure of the semi-coke deposits exhibits considerable variation probably due to both physical and chemical separation during deposition of the sediment and to different diagenetic/hydration processes. Surface layers are leached by continuous rainfall, which lowers the pH of porewater in the upper layers and thus initiates the dissolution of ettringite. Elevated content of carbonates and respectively lower amount of terrigenous material at the foot of the waste mound can be explained by gravitational fractionation during the dumping of the material, with large and hard partially decomposed limestone particles transported onto the foot area of the mound. That is also reflected in the mineral composition of the sediment.

**Poolkoksi mineraloogiline koostis VKG Õlitööstuse AS jäätmemäe
näitel, Kohtla-Järvel.**

Riho Mõtlep

Eesti kaevandatavast põlevkivist kasutatakse ligikaudu 20% keemiatööstuses põlevkiviõli tootmiseks. Ühe tonni põlevkivi tootmisel tekib kuni 3 tonni tahkeid jäätmeid, mis valdavalt koosnevad termiliselt töödeldud ja kuni 10(16)% orgaanilise ainese jääksisaldusega põlevkiviräbust – nn poolkoksist. Tekkiva poolkoksi taaskasutus on piiratud ja absoluutselt valdav osa poolkoksist ladestatakse setteplatoodele. Tänapäevaks on ladestatud kogused ületanud 100 miljoni tonni piiri. Poolkoksi käsitletakse ohtliku jäätmena tänu selles leiduvatele orgaanilistele komponentidele. Vaatamata rohketele aastakümnete jooksul valminud uurimustele ei ole meile teadaolevalt spetsiaalselt uuritud poolkoksi mineraalset koostist ja selle kujunemist. Samas on need küsimused tähtsad poolkoksi moodustumise protsessi, kui ka selle ladestatud sette kujunemise, püsivuse ja keskkonnaohtlikuse seisukohalt.

Käesoleva magistritöö eesmärgiks oli selgitada poolkoksi mineraalne koostis, selle kujunemine ja hilisem diagenetiline transformeerumine OÜ Viru Keemia Grupp poolkoksiplatool Kohtla-Järvel. Uurimuse tulemused näitavad, et värske, hüdratiseerumata poolkoksi mineraalses koostises domineervad põlevkivi algsest koostisest pärinevad mineraalid – kaltsiit, dolomiit, kvarts, K-päevakivi ja savimineraalid, mille kõrval esinevad utmise käigus toimunud primaarsete mineraalide lagunemisel ning reageerimisel tekkinud autigeensed faasid nagu oldhamiit (CaS) ja klinkrimineraalid (beliit, merwiniit, meliliit ja periklaas), mis on moodustunud utmise viimases kõrgetemperatuurilises faasis. Poolkoksi ladestamisel jäätmeplatoodele toimub materjali hüdratiseerumine, mille käigus kaovad ebastabiilsed sekundaarsed faasid (nt. oldhamiit) ja moodustub märkimisväärsel kogusel (kuni 30%) autigeenset Ca-Al-sulfaati – ettringiiti. Poolkoksi mineraalne koostis jäätmeplatool lasundis on suhteliselt stabiilne ja jälgitavad muutused on seotud ettringidi osalise lahustumisega pinnakihtides ja algse settematerjali separeerumisega ladestamisel.

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