TECHNOGENIC MINERALS IN THE WASTE ROCK HEAPS OF ESTONIAN OIL SHALE MINES AND THEIR USE TO PREDICT THE ENVIRONMENTAL IMPACT OF THE WASTE

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The newly formed minerals inside the waste rock heaps of Estonian oil shale mines were studied using X-ray diffraction analysis and scanning electron microscopy. In the unburnt heaps, the only detectable new solid phases were ferric oxyhydroxide and gypsum. In the burnt heaps, however, a large number of technogenic minerals were found, including lime, periclase, portlandite, brussite, calcite, aragonite, leucite, diopside, gehlenite, wollastonite, anhydrite, ettringite, hematite, tobermorite, larnite and spurrite.

The reasons for spontaneous combustion include heap size and shape, but importantly also the heterogeneities, especially gravitational fractionation of the rocks during the disposal. The areas where the shale remains not fully oxidised were found, characterised by the presence of oil in the surface layer and layers of amorphous carbon on the waste rock lumps. The negative environmental impacts of the burnt heaps, including leachate with high alkalinity and sulfate content, as well as oil plumes, may become evident after decades after burning only, because the temperature inside the heaps decreases very slowly.

Introduction

Estonian oil shale mines produce kukersite for processing and power generation. In all of these operations, large amounts of solid residues are produced. About a third of the rock mass excavated by underground mining is the waste rock, separated during enrichment and disposed in heaps with the height of several tens of meters. The mining peaked in early 1980's when about 7-8 Mt waste rock was disposed each year. By 1998, about 200 Mt of the waste rock was disposed in heaps.

In order to understand the impact of the waste rock on the environment, the study of the solid phases of the waste is needed. These solid phases are here named the technogenic minerals, although the

process of generation of many of them is analogous to the natural geological processes, such as thermal metamorphism and chemical sedimentation from oversaturated water solutions. The technogenic minerals and their changes in time determine the quality of the leachate leaking from the waste, with the possibility of being directly responsible for water pollution.

The mineral composition of the kukersite waste has not been a subject of an extensive research. The reason is that the waste rock undergoes small chemical changes only, mainly because of the oxidation of pyrite, without causing serious environmental problems. So, the composition of the waste rock is approximated to the unchanged shale and limestone. However, some of the waste rock heaps have suffered spontaneous combustion, totally changing the composition of solids.

The aim of this study was to document the solid phase composition of the altered waste rock, especially that of the burnt heaps, together with the geochemical analysis of the processes of change. The study assists to work out the guidelines on the hazardousness and water pollution potential of the waste rock.

Materials and Methods

The samples of the waste rock were taken and analysed by means of X-ray diffraction during 1988-1998. The XRD data were collected scanning unoriented powdered samples with DRON-0.5, DRON-3M and Siemens diffraction systems using FeKα and CuKα radiation. The mineralogy of the unchanged oil shale was analysed quantitatively using the methods described by Utsal in 1984 [1]. The sample of the black surface layer from the Kukruse burnt waste rock heap was also analysed using PHILIPS XL30 scanning electron microscope, equipped with the energy dispersive spectrometry system. The computer code PHREEQC [2] and the Wateq4 database [3] were used to characterise some geochemical interactions in the water phase.

Mineralogy of Kukersite

Kukersite is at present the only economically used oil shale in Estonia and belongs to the general category of carbonate-rich shales. The organic matter is yellowish-brown to dark-brown kerogen containing algal remains with the size between 10-40μm [4]. Values of the kerogen content of productive seams are ranging between 30-60 %.

The estimations of the mineral composition calculated for 48 samples from different kukersite seams of the mining area of *Aidu* opencast mine are presented in Table 1. The main carbonate mineral is calcite. Dolomite occurs in subordinate amounts, usually not exceeding 5 %. Close to deep faults, however, dolomite has often replaced nearly all the calcite [5]. The terrigenous component is presented by silt-size quartz, feldspar and clay minerals - illite with traces of chlorite. The content of pyrite is 1-3 %.

*Table 1.* **Main Minerals and Kerogen, and Their Content in Productive Seams A-F of Kukersit (Dry Weight)**

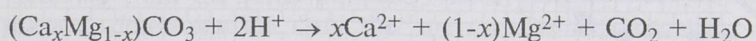| Mineral	Formula	Wt% range	Average	Mol per 1 kg
Quartz	SiO_2	3-11	4.8	0.80
Orthoclase	$KAlSi_3O_8$	1-5	3.1	0.11
Illite	$K_{0.6}Mg_{0.25}Al_{2.3}Si_{3.5}O_{10}(OH)_2$	4-17	9.1	0.24
Chlorite	$(Mg,Fe^{2+},Fe^{3+})_6 \cdot AlSi_3O_{10}(OH)_8$	0-2	0.4	≈ 0.01
Pyrite	FeS_2	1-3	1.6	0.13
Calcite	$CaCO_3$	25-50	39.0	3.9
Dolomite	$CaMg(CO_3)_2$	0-5	1.7	0.092
Kerogen	(Mol%) C 39, H 57, O 3.8, N 0.18, S 0.39	32-52	40.3	

Formation of Technogenic Minerals

Unburnt Waste Rock Heaps

The waste rock contains 3-6 % of kukersite [6], the remainder being limestone originating from the layers intercalating with the kukersite seams. The main chemical reaction inside the waste rock heaps is oxidation of pyrite, followed by the buffering of the acidity by limestone, precipitation of ferric oxyhydroxide and, in the case of high amount of pyrite oxidised per kg of available water (>0.008 mol/kg, [7]), also gypsum. The buffering reaction is fast and no acidification is caused, as the amount of calcium and magnesium carbonates available exceeds the amount that is needed to buffer the acidity by about 400-800 times. Eventually, the carbonate content of kukersite itself exceeds the needed amount 10-20 times. The leachate of the waste rock heaps is, therefore, slightly alkaline (pH 7.5-8.5), with Ca^{2+} and Mg^{2+} being the main cations, and HCO_3^- as well as SO_4^{2-} the main anions. The main reactions are:

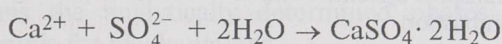(1) Oxidation of pyrite and precipitation of ferric oxyhydroxide:

$$FeS_2 + 3.75O_2 + 3.5H_2O \rightarrow Fe(OH)_3 + 4H^+ + 2SO_4^{2-}$$
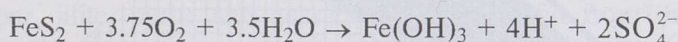
(2) Buffering of the acidity by carbonates in limestone ($x > 0.75$ for calcite and $x \approx 0.5$ for dolomite):

$$(Ca_xMg_{1-x})CO_3 + 2H^+ \rightarrow xCa^{2+} + (1-x)Mg^{2+} + CO_2 + H_2O$$

(3) Dissolution of carbonates by CO_2:

$$(Ca_xMg_{1-x})CO_3 + CO_2 + H_2O \rightarrow xCa^{2+} + (1-x)Mg^{2+} + 2HCO_3^-$$

(4) Precipitation of gypsum:

$$Ca^{2+} + SO_4^{2-} + 2H_2O \rightarrow CaSO_4 \cdot 2H_2O$$

Burnt Waste Rock Heaps

The main reason why a waste rock heap starts to burn is spontaneous combustion, caused by too steep slopes, too large height of the heaps, as well as too big proportion of the oil shale within the waste rock. The role of the heterogeneities has also to be considered [8]. Although the average concentration of pyrite is very small in the waste rock (0.05-0.1 %), it might become a significant trigger of the initial temperature rise, if the shale is concentrated during the disposal by gravitational forces.

Figure 1 presents schematically various stages in the heap formation. In stage 1, the waste rock is deposited through dropping from the certain height. The kukersite lumps are desintegrated much easier than limestone. Therefore, the gravitational fractionation occurs, with the fraction with largest particle size and permeability, as well as highest concentration of limestone accumulating in the foot (base) area (zone 1 in Fig. 1). Zone 2 is the "intermediate" one, and in zone 3, the waste rock with smallest particle size and therefore largest oil shale content, as well as lowest permeability, accumulates. In stage 2, the transport road is continuously extended and the fractionation occurs along the new slope.
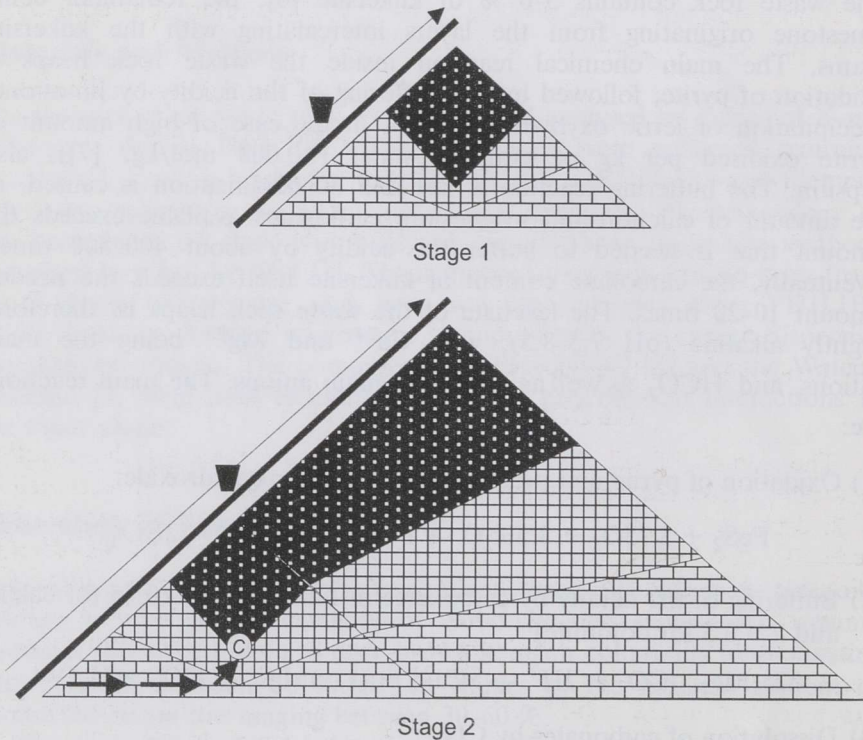
Stage 1

Stage 2

Fig. 1. Formation of a waste rock heap containing oil shale and limestone.
Stage 1: disposal from the transport system; Stage 2: disposal through continuous extension of the transport system; Point C − the most probable point for the start of spontaneous combustion

Regarding spontaneous combustion of the heap, the area C in Fig. 1 is the most critical one. Firstly, the concentration of fine-grained oil shale is so large that fastly oxidising fine-grained pyrite may serve as a trigger for the initial temperature rise, increasing the temperature of the waste rock to the region where the organic matter starts to oxidise at high rate. Secondly, the formation of convective air currents is supported by the high permeability zone below. And thirdly, as the shale is deposited in C first, the incubation period should end there also first.

During 1960's and until mid-70's, seven heaps including altogether 6 Mt of the waste rock combusted spontaneously and burned. The average burning time was about ten years and no methods of extinguishing were successful. The improvements in disposal technology and better enrichment of the shale have guaranteed that no new heaps have been burning during 1980's and 90's, with the exception of the fires in the old *Küttejõu* open pit, where the waste containing oil shale has been ignited several times.

The surface layers of three of the burnt heaps were sampled and a drill core material of a burnt heap of *Sompa* mine was analysed. The main chemical reactions in the surface layer are connected with the decomposition of carbonates into oxides and, after the cool-down, formation of hydroxides and again carbonates:
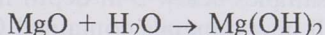
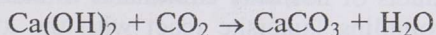(5) Decomposition of carbonates into lime (CaO) and periclase (MgO):

$$(Ca_xMg_{1-x})CO_3 \rightarrow xCaO + (1-x)MgO + CO_2$$
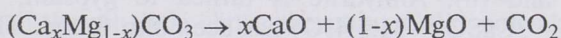
(6) Hydration of lime and formation of portlandite:

$$CaO + H_2O \rightarrow Ca(OH)_2$$
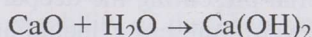
(7) Hydration of periclase into brussite:

$$MgO + H_2O \rightarrow Mg(OH)_2$$

(8) Reaction of portlandite back to calcite:

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$$

The lumps of oil shale in the waste heaps undergo the reactions between carbonate and silicate phases. The reaction between calcite, K-feldspar, illite, pyrite and quartz, as well as sulfur from the kerogen, leads to the formation of technogenic minerals leucite ($KAlSi_2O_6$), diopside ($CaMgSi_2O_8$), gehlenite ($Ca_2Al_2SiO_7$), wollastonite ($CaSiO_3$), anhydrite ($CaSO_4$), hematite (Fe_2O_3) and lime (CaO). All these minerals were detected from the XRD patterns. These patterns were not used for quantitative determination of the new minerals because of the uncertainties in the coefficients of the characteristic peak intensity ratios and poor crystallinity of the minerals. The approximate concentrations of these minerals, however, can be calculated on the basis of the approximate molal concentrations of the primary minerals (Tables 1 and 2). The number of the newly formed phases that were detected (seven) corresponds to the number of the main chemical compounds available in the system, thus the analytically determined phases can be taken as "nominal" minerals for recalculations.

Table 2. **Calculation of New Minerals Formed during Burning of Kukersit in the Surface Layer of the Waste Rock Dumps (on the Basis of an Average Kukersit Sample)**

Minerals	Average kukersit sample (mol/kg)							M_r	Wt%
	CaO (4.0)	MgO (0.15)	Al_2O_3 (0.33)	SiO_2 (2.0)	K_2O (0.13)	Fe_2O_3 (0.07)	SO_3 (0.52)		
Leucite $KAlSi_2O_6$			0.13	0.50	0.13			162	9.4
Diopside $CaMgSi_2O_8$	0.15	0.15		0.30				217	7.5
Gehlenite $Ca_2Al_2SiO_7$	0.41		0.20	0.20				274	12.6
Wollastonite $CaSiO_3$	1.0			1.0				116	26.8
Anhydrite $CaSO_4$	0.52						0.52	136	16.4
Hematite Fe_2O_3						0.07		159	2.4
Lime CaO	1.92							56	24.9

After cooling, lime is turned to portlandite and a carbonate phase (either calcite or aragonite, another modification of $CaCO_3$), as given by reactions (6) and (8). Anhydrite is turned to gypsum, but ettringite ($3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 31.5H_2O$) has been also found. The presence of $MgCO_3$ has not been detected.

In the drill core material presenting the deeper parts of the burnt heap, some other minerals were present, including larnite (β-Ca_2SiO_4), tobermorite ($4CaO \cdot 5SiO_2 \cdot 5H_2O$), periclase ($MgO$) and spurrite ($Ca_5Si_2O_8CO_3$). In the samples below 5 m depth in the drill core from the top of a conical heap, all new minerals contained Ca except periclase. The possible explanation is, that at higher temperature conditions, the decomposition products of not only carbonates available in kukersite, but also limestone surrounding kukersite react with the kukersite lumps that leads to the total domination of Ca and Mg compounds in the mixture.

The "Black Blocks" Zones

On the southern slope of the Kukruse burnt heap, the local conditions differing from other parts of the heap and from the other heaps were found. Twelve years after the burning was considered to be ended, the surface temperature in this area was still 50 °C, the pores of the surface layer partly saturated with the shale oil and the vegetation was destroyed. Obviously, the process of semicoking was still continuing inside the heap. Chesnokov et al. [9] have described similar zones and formation of graphite layers on the waste rock lumps in waste rock heaps of Chelyabinsk coal basin, naming these zones as "black blocks". In the flow channels of the hot gases onto the surface, the lumps of limestone were covered with the layer of amorphous carbon (Fig. 2). Also, cylindrical forms of the same material with the length of up to 10 mm and diameter of 0.10-0.15 mm were detected.
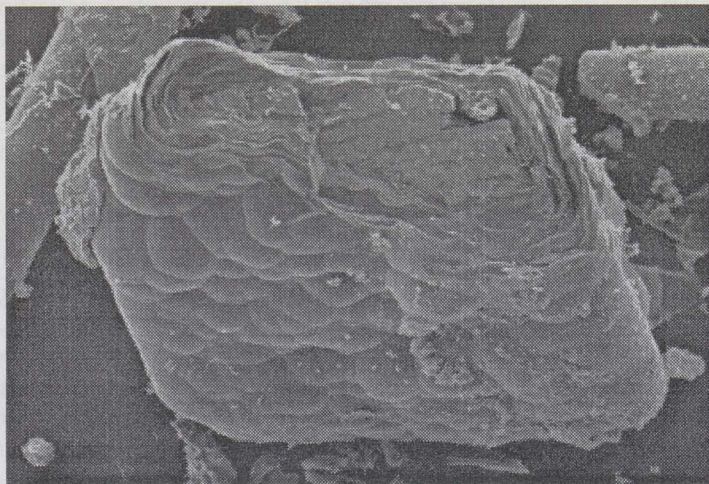
Fig. 2. Scanning electron micrographs of the amorphous carbon cover layer consisting of sub-layers

The formation of the Kukruse heap was analogous to that depicted in Fig. 1, with transport road approaching from the south. Thus, the area of point *C* in Fig. 1 matches with the area of "black blocks" of the Kukruse heap. Possibly, all the oil shale above the point *C* did not take part in the oxidation process, as the hot gases were transported out through that material with no oxygen present, leading to the oil production. Also, at high temperatures, the permeability of the heap slope could be decreased. In the period of overall cooling of the dump, the process of semicoking still continues, generating oil and forming the layers of amorphous carbon.

Environmental Impact of the Burnt Heaps

According to the hydrochemical analysis using computer code PHREEQC, the mineralogical composition of the burnt heaps gives a reason to suppose that the leachate flowing out of the heaps could be highly alkaline (pH up to 12.4) and also with high sulfate content, as portlandite and gypsum are the most soluble minerals among these described in this study. However, the temperature in the deeper layers stays high for a very long time and should be monitored in order to understand the long term impacts. From the borehole that was drilled 12 years after the last burning evidence in Sompa, the temperatures up to 240 °C were measured at the bottom of the hole (depth 23 m). Hence, the infiltrating water either evaporates or is used up in hydration reactions during decades after burning, explaining also the formation of tobermorite. Therefore, the period when the alkaline leachate begins to be produced might be even longer, of the order of a couple of decades after the end of burning.

The burnt heaps include zones where kerogen of kukersite is not totally oxidised and the shale oil is still present. This should be considered when the plans of the use or mass movement of the waste rock is planned. Also, the movement of oil plumes may contaminate the ground water resources.

Conclusions

1. The main geochemical reaction in the unburnt heaps is oxidation of pyrite, and the only new solid phases detected were ferric oxy-hydroxide and gypsum. In the samples from the burnt heaps, a large number of technogenic minerals were found, including lime, periclase, portlandite, brussite, calcite, aragonite, leucite, diopside, gehlenite, wollastonite, anhydrite, ettringite, hematite, tobermorite, larnite and spurrite.

2. The geochemical calculations made on the molal basis of the unchanged and burnt kukersite indicate that the analytically determined minerals can be used as the "nominal" minerals describing the character of change.

3. The phenomenon of amorphous carbon formation in the "black blocks" zone together with the abundance of oil in the surface layer are evidences that not all of the kukersite is fully oxidised. The formation of the "black blocks" in certain areas can be explained by the gravitational fractionation of the waste rock material during disposal.

4. The negative environmental impact of the burnt heaps may become evident after decades after burning only, because the temperature inside the heaps decreases very slowly and practically no leachate is formed. The potential problems are connected with high alkalinity, sulfate content, as well as with migration of oil plumes.

Acknowledgements

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