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## OXIDATION OF DICTYONEMA SHALE IN MAARDU MINING WASTE DUMPS

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*Geochemical processes occurring in Maardu mining waste rock dumps, Estonia, are reviewed on the basis of Estonian practice and recent modelling studies. Oxidation of Dictyonema shale disposed close to the steep slopes leads to air pollution and destruction of newly formed vegetation during first decades after disposal. New mineral phases are formed at high temperatures and potential pyritic acidity is eliminated. In central parts of the dump, low-temperature (below 40 °C) oxidation of pyrite leads to a sequence of geochemical reactions in interaction with dumped material, including conversion of illite to smectite, precipitation of K-jarosite, gypsum and ferric oxyhydroxide, as well as formation of leachate with high sulphate content and anomalously high Mg/Ca ratio.*

*Hydrochemical modelling showed that low-temperature oxidative leaching of the shale would cause regional surface and ground water contamination with sulphate for centuries. A possibility exists, that limestone buffering capacity becomes locally depleted inside the dump, leading to the breakthrough of acidic and metal-rich waters. Maardu study assists also in development of environmentally friendly technology for shale handling in future.*

## Introduction

Geochemical processes, occurring when Dictyonema shale is exposed to the atmosphere, have been one of the most relevant environmental issues in Estonia during the last two decades. In late 1980's, the negative environmental experience of Maardu mining waste dumps triggered the public protest against the decision of Soviet regime administrators to establish new opencast phosphorite mine in Toolse. The so-called phosphorite war grew into National front movement and finally led to the declaration of Estonian independence in 1991.

Dictyonema shale is a brownish to black porous sedimentary rock (average pore size 1-5  $\mu\text{m}$ ) that contains grains of three main minerals (quartz, sanidine type potassium feldspar and illite), as well as kerogeneous organic matter, pyrite and high concentrations of a range of heavy metals (U, Mo, V, Pb, Cu, Ni, Zn) [1-5]. Although the shale, the layer of which made up a significant part of the phosphorite ore overburden, was historically known as a material capable to combust spontaneously [6], no attention was paid to account for this phenomena in 1964 when *Maardu* opencast was established - almost 50 years had passed since the shale fire in Harku near Tallinn [6, 7].

Although the first hot spots occurred after a couple of months already, these did not hinder the mining operations because the environmental concerns were out of the scope at that time. Only in 1982, the attempt was made to avoid spontaneous combustion by disposing the shale selectively as a layer and covered by porous rock lumps and sediments [8, 9]. It will be shown in this paper, that even this technology did not take into account the complexity of the combustion process. Furthermore, regarding low-temperature oxidation of the shale pyrite, where sulphuric acid is produced, the selective disposal may produce significantly greater hazards in long term.

The total area of Maardu dumps is 10.6  $\text{km}^2$ , every square meter containing on the average 7 tonnes of the shale opened to the access of atmospheric oxygen. Thus, the water quality in Maardu dumps and in surroundings is dictated by dissolved oxidation products of the shale and their interaction with surrounding rocks. Except gaining the knowledge about negative impacts of Maardu dumps, the study of the processes in Maardu assists to work out guidelines for economically effective and environmentally friendly technology for shale disposal, if new phosphorite mines are planned.

The aim of this paper was to combine the experience of the Institute of Chemical and Biological Physics (KBFI) of the Estonian Academy of Sciences and the recent modelling results of the dump processes at the Stockholm Royal Institute of Technology (KTH), Sweden. The overview about the site development and study history is given, the current state-

of-art described, main mistakes discussed, guidelines for shale disposal proposed, and significant but still unclear problems defined.

## Study History and Site Development

Spontaneous heating of fossil fuels and sulphidic rocks are common phenomena in nature. Fossil fuel fires have been reported thousands of years ago already, with some of these lasting for a very long time. For example, the fire in a coal deposit at Yagnob valley, Tadjikistan, that was still observed in 1970's, was first described in the works of Pliny the Elder (23-79 AD) [10].

In the 16th century, Georgius Agricola recognised the possibility to use increased ground temperature as an indicator to find sulphide ore deposits [11]. The capability of Dictyonema shale to combust spontaneously was first reported in 1791 by J. G. Georgi [12]. The shale burnt several times in the 19th century, when the erosion of the North Estonian Klint led to the formation of slump sediments containing the shale, as well as in the offshore bars on the North Estonian coast [6, 7].

After World War II, the chemical composition, physical and chemical properties and thermal destruction of Estonian Dictyonema shale were studied extensively at the Institute of Chemistry, the Estonian Academy of Sciences [13-17]. Based on these data, the studies of spontaneous combustion were started when the first hot spots occurred in Maardu dumps in mid 1960's [18-21]. These were, unfortunately, mainly laboratory experiments using methodology recommended by Stadnikov [22], and did not account for transport processes in real dumps.

During the first decades of waste rock disposal in Maardu, no environmental and landscaping considerations were taken into account, resulting in formation of uneven, moundy artificial landscape. Formation of hot spots was favoured by the delay in the revegetation program. In 1976, the studies of the spontaneous combustion process and distribution of hot spots in Maardu were started at the Geological Survey of Estonia. Temperature measurements were made and shale samples taken for investigation of the combustion, based on the methods developed by Veselovsky [23-26]. The methods can be used to predict the change in air composition in closed and partially closed systems [27-29]. The results of these investigations are summarised in the reports of the Geological Survey of Estonia [30-32].

Also in 1976, a new disposal technology to avoid spontaneous combustion was recommended to the mining company *Eesti Fosforiit* in the report of the Technical Institute of Novocherkassk (Russia). It involved the removal of the shale layer selectively. The shale was endorsed to be disposed as a separate layer in the mined-out area and to be covered with porous non-oxidative overburden material. Similar

recommendations were given by GIGHS (USSR State Institute of Industrial Ores) and were used at the site from 1982 [8, 9]. The disposal scheme included the establishment of 1-2 m thick layer of limestone lumps below the 4-6 m layer of the shale covered by other overburden material (limestone, sandstones, quaternary sands, and moraine). Even this way of disposal, however, did not avoid the formation of hot spots close to the steep trench slopes.

During 1980-1993, various research institutes of the Estonian Academy of Sciences (KBFI, Institute of Geology, Institute of Chemistry) contributed separately to the shale oxidation research. The problem was assessed from a historical point [6, 7], the temperature distribution inside the dumps was monitored [33], the concept of maximum permissible and critical temperature of spontaneous combustion introduced [34], the sulphate pollution investigated [35-37], and the experiments made to simulate oxidative leaching of the unweathered shale and shale ash [38-40].

The accumulation of heavy metals in the dump plants [36] and formation of new precipitates in the hot spot area [41] were also observed. Despite the importance and actuality of the problem, the shale research remained uncoordinated and was stopped in 1993 because of the peculiarities of the environmental movement and the change in general directions of scientific research in Estonia.

Economically feasible and environmentally exploitable phosphorite reserves in Maardu were depleted by 1991. Seven waste rock plateaus separated by trenches were left. About 7.9 km<sup>2</sup> is uneven and covered by waste rock mounds, and 2.7 km<sup>2</sup> levelled, consisting of selectively disposed material. The South Dump (2 km<sup>2</sup>) is separated from the North Dump by Tallinn-Narva motorway. The hydrological systems of these dumps are isolated and the water table in the South Dump has risen during the last years, thus the selectively disposed shale layer is presently located below the ground water table. In Northern Dump, most of the trenches have remained dry. The revegetation program of the site has been accomplished. In areas, however, where the shale was disposed directly on the surface, the vegetative cover is poor.

In 1993, the research project concerning the complexity of Maardu problems was started at the Department of Chemical Engineering, Stockholm Royal Institute of Technology. In co-operation with the Institute of Geology of Tartu University, the research was concentrated on mathematical modelling and quantitative estimation of the multiphase reaction and transport processes. Sweden is among the countries facing analogous problems, for example oxidation of pyrite in the alum shale tailings in the Ranstad area [42] and mining waste rock in Aitik [43], as well as spontaneous combustion of materials deposited on the ground surface [44].

The details and the results of hydrochemical modelling, analysed briefly in this paper, are provided in the publications of the first author [45-47]. The second author contributed with field experience and the ideas of the Russian Veselovsky school of spontaneous heating and combustion of piled materials, especially underlying the heterogeneity of the material after disposal and the formation of hot spots as important factors in dump performance and, subsequently, in model development.

## Spontaneous Combustion in Maardu Dumps

The Estonian Dictyonema shale deposited originally as organic-rich mud in Early Ordovician (Tremadocian) sea about 495-485 million years ago. The shale contains two different oxidising compounds - pyrite and kerogeneous organic matter (in Maardu shale, 4-6 % and 15-20 %, respectively). Laying in sedimentary bed and covered by sediments and rocks, the clayey shale forms a low permeability layer and the shale has remained unoxidised over hundreds of millions of years. Eroded until to the connection with atmosphere or opened during the mining activities, however, microcrystalline pyrite dispersed in the shale [47] starts to oxidise at high rate generating heat.

In moist conditions and low temperatures (below 30 °C), the rate of pyrite oxidation was observed to be orders of magnitude higher than that of kerogeneous organic matter. In the shale lumps weathered on the dump surface no microcrystalline pyrite was found, whereas the organic matter had oxidised in the 0.1-0.5 mm thick cover layer of the lumps only [47]. This finding is supported by the study of natural outcrops of the shale where the shale layer is covered by secondary minerals containing Fe(III) and sulphates [48]. In the temperature region 45-60 °C, the oxygen consumption rate of the shale increases stepwise [34]. This phenomenon is connected with the increase in kerogen oxidation rate. Thus, in favourable conditions, pyrite oxidation is triggering the active oxidation of kerogen.

## Favourable Conditions for Spontaneous Combustion

The key issue in understanding the spontaneous combustion process in the dump is to define, what are these 'favourable conditions' under which the heating proceeds to combustion. Exothermal oxidation reactions lead to spontaneous heating, but not necessarily to combustion. The main conditions that have to be fulfilled for spontaneous combustion are:

- (1) Sufficient amount of material per volume unit of the waste rock, that oxidises at high rate in the presence of oxygen (the reactivity with respect to oxygen is high)
- (2) Sufficient influx of oxygen transported to the oxidising material

(3) Slow removal rate of produced heat from oxidation centres to surroundings

If even one of those conditions is not satisfied, spontaneous heating and combustion do not occur [23]. The weathering proceeds without substantial increase in the temperature of the waste rock.

### Reactivity of Oxidising Materials

The reactivity of oxidising materials with respect to atmospheric oxygen can be experimentally assessed by finding the average value of the kinetic constant of oxygen consumption  $U_s$  ( $\text{cm}^3 \text{m}^{-2} \text{h}^{-1}$ ) that is measured during the 250 h experiment according to the method developed in the Skotchinsky Institute of Mining Engineering of the Russian Academy of Sciences [23-26, 32]. The results obtained using this method can be directly used in engineering calculations [34].

The constant is temperature dependent. Below the critical temperature region, the temperature rise  $10^\circ\text{C}$  of the Dictyonema shale is followed by the increase in the constant by the factor of 1.7-1.8. The experiments of shale oxidation showed that the critical temperature  $t_{kr}$  ( $^\circ\text{C}$ ), starting from which the temperature increase is fast, was inversely proportional to the reactivity  $U_s$  with values  $t_{kr} = 40^\circ\text{C}$  at  $U_s = 2.5 \text{cm}^3 \text{m}^{-2} \text{h}^{-1}$  and  $t_{kr} = 35^\circ\text{C}$  at  $U_s = 4.1 \text{cm}^3 \text{m}^{-2} \text{h}^{-1}$  [34].

Inside the heterogeneous Maardu dumps, the rate, at which a certain waste rock volume oxidises in the case of free oxygen access, is presumably mainly the function of the particle size distribution and the volumetric density of the shale. The extent of the period, after which the critical temperature is reached, depends on the initial temperature of the waste rock and is, therefore, a function of air temperature and presence of snow and ice during the disposal.

In Maardu site, about 34-38 % of the waste rock is Dictyonema shale. The oxygen initially available inside the dump (about 21 % of the gas-filled pore volume) has a capacity to oxidise stoichiometrically about 240-300 g of pyrite per  $\text{m}^3$  of waste rock with respective heat production 3.2-4.0  $\text{kJ m}^{-3}$  and, even if heat is not transported out from the dump, temperature rise of less than  $2^\circ\text{C}$  is expected. Obviously, for oxidation reaction to proceed, additional oxygen has to be transported into the dump by different mechanisms. At the same time, oxygen initially present in the dump oxidises only about 1 % of the shale pyrite. Hence, pyrite oxidation has the potential to trigger the spontaneous combustion, rising the waste rock temperature to the region, where oxidation reactivity of kerogen is high.

## Physical Conditions

Whether the potential of the waste rock to heat substantially and combust spontaneously is realised or not, depends on the physical conditions inside the dump, as well as climatic conditions, such as ambient air temperature, air pressure, wind direction and speed, and character of precipitation and evapotranspiration. In some cases, the variations in these conditions are also important to account for.

Regarding the internal physical conditions, dump porosity, permeability, moisture content and the shape of the surface are most important to account for. In general, spontaneous combustion is characteristic of the organic-rich dumps with high gas-filled porosity and high permeability, although the moisture content is also important, as the oxidation reaction at low temperatures proceeds in the presence of water. The shape of these dump areas necessarily includes steep slopes.

The oxidation of organic matter is triggered by the temperature increase, caused by exothermal reaction of pyrite oxidation. Thus, the results of the numerous studies conducted on oxidation of pyritic heaps can be directly adopted to describe the processes inside Maardu dumps, until the critical temperature is achieved.

## Pyritic Phase of Dump Oxidation

As the shale pyrite is microcrystalline and, therefore, rapidly oxidising relative to the oxygen supply rate, the oxidation is rate-limited by oxygen transport processes [49, 50]. If the dump surface is horizontal without steep slopes and no large cracks present, the main way in which oxygen is supplied into the dump is the diffusion in gaseous phase, driven by concentration gradient. The diffusional flux can be estimated according to the Fick's law and this estimation is the basis of pyrite oxidation calculations [45, 51-59].

The parameter with largest uncertainty is effective diffusion coefficient  $D_{eff}$ , depending on porosity, tortuosity and water saturation index of the dumped material. If the distribution and reactivity of the reactant, as well as effective diffusivity are homogeneous, there is no concentration gradient of oxygen in horizontal dimensions and the one-dimensional form of oxygen flux towards the dump depth is expressed simply as

$$N_{O_2} = D_{eff} \frac{\Delta c}{\Delta z}$$

where  $\Delta c/\Delta z$  is the concentration gradient of oxygen, assuming that the oxidation front is located at depth  $z$ .

In practice, the sharp oxidation fronts do not develop and the oxidation proceeds as a zone, depending on the chemical pyrite oxidation rate and diffusional transport of dissolved oxygen through water saturated

pyritic fragments or oxidised layers, formed on pyrite crystal surfaces. This is also accounted for in the models [45, 51-59].

The main way, in which produced heat is removed from the dump, is thermal diffusion through solid waste rock. The shale disposed on the dump surface does not heat significantly, as the rate at which the shale is cooled by atmosphere is higher than that released by the chemical reaction, in which the heat is produced. Therefore, hot spots of spontaneous combustion occur at some critical distance from the dump surface only, although the process may proceed towards the surface. The effective diffusivity and thermal conductivity may vary considerably in pyritic dumps. They counterbalance each other, however, as the function of depth (if the oxidation front is closer to the surface, the oxygen concentration gradient is high, but so is the thermal diffusion gradient). Using average parameters for the pyritic partially saturated dumps it is evident that diffusion on its own is unable to cause the temperature rise of the pyritic waste rock in Maardu to the critical region [60].

These calculations are in agreement with thermal monitoring data of the dump areas, not located close to the slopes [33]. At the same time, the diffusion of oxygen does have the triggering function in spontaneous combustion. It causes a small temperature rise inside the dump, leading to the formation of convective air currents inside the steep slopes. The driving force (buoyancy force) of these free convection currents is the density gradient of the air, as density is the function of temperature [49, 50].

### **Spontaneous Combustion Phase**

From oxygen and heat diffusion calculations it is evident that the main condition to be satisfied for the temperature increase to the critical region is the presence of steep slopes, through which convective air currents enter the dump. The free convection caused by temperature increase during pyrite oxidation is, however, only one of the potential causes of air currents. These currents occur also as the result of daily and seasonal temperature variations. Also, the prevailing direction and speed of wind has to be accounted for [61] and oxygen is transported by the changes in air pressure [62]. The significance of all these mechanisms is usually limited to the slope area.

If the temperature reaches the critical value, the free convection air currents begin to dominate. The velocity of the air current is a function of the temperature difference between dump pore gas and the atmosphere. With increasing temperature, the velocity of the air current increases also. Inside the hot spots in Maardu, the temperatures as high as 800-1200 °C have been measured [63].



## Formation of Hot Spots in Maardu

In order to explain the location of hot spots observed in Maardu and find potential new locations, it is necessary to review the mining and disposal technology. These can be generally divided into two periods.

During the first period (1964-1982), the shale was disposed randomly and no attention was paid to levelling up the surface. The usual way was to dump the overburden by dragline as mounds. When dropped, the waste rock fractionated gravitationally with largest particles (mainly limestone as the hardest compound) concentrating in the lower and small shale particles in the upper part (Fig. 1).

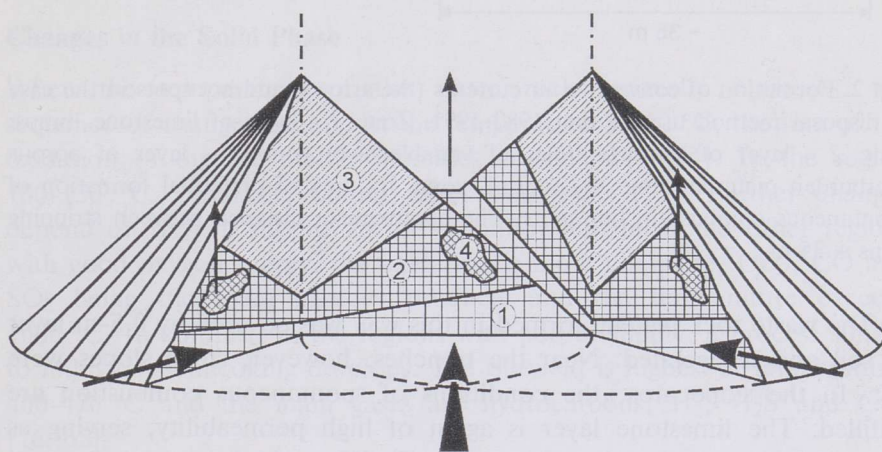


Fig. 1. Formation of convective air currents (the arrows) and hot spots in the case of disposal method used during 1964-1982. Zone 1 - lumpy waste rock with high permeability, mainly limestone; zone 2 - intermediate particle size fraction with high permeability and high shale content; zone 3 - fine particle size fraction with low permeability and high shale content; zone 4 - area of preferential formation of spontaneous combustion hot spots

The regions of high permeability and low shale oxidation reactivity, mainly containing limestone and big shale lumps, were formed in the foot area (zone 1). In zone 2, both permeability and oxidation reactivity of the shale fraction 5-30 mm are high. In zone 3, the oxidation reactivity of the shale is high, but permeability low, as it contains small shale particles mixed with sand, formed during destruction of sandstone. We have observed that the hot spots develop primarily in the zone 2, and especially when neighbouring mounds are in connection. The formation of convective air currents is supported by high permeability zone below (Fig. 1). If the hot spots are formed, the combustion process may proceed evolving the whole mound.

During the second period (1982-1991), the 4-6 m layer of mainly lumpy shale was disposed on the 1-2 m layer of limestone lumps, that was expected to act as geochemical barrier for acidic water. The shale layer was covered by remaining overburden, including sandstones, limestone and quaternary sediments (Fig. 2).

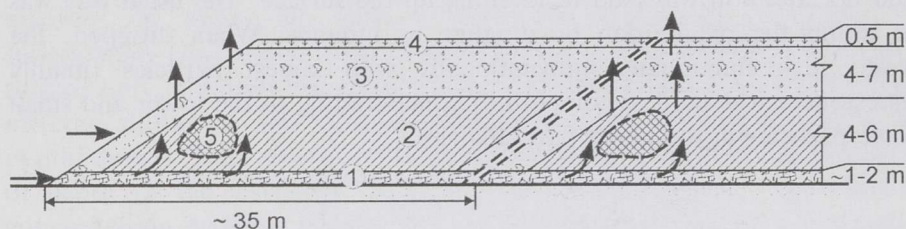


Fig. 2. Formation of convective air currents (the arrows) and hot spots in the case of disposal method used during 1982-1991. Zone 1 - layer of limestone lumps; zone 2 - layer of shale particles of variable size; zone 3 - layer of porous overburden material; zone 4 - topsoil, zone 5 - area of preferential formation of spontaneous combustion hot spots. The approximate distance between stripping steps is 35 m

The waste rock plateau formed in this way was covered by 0.5-m layer of soil and revegetated. Near the trenches, however, steep slopes were left. In the slope area, the conditions of spontaneous combustion are fulfilled. The limestone layer is again of high permeability, serving as channel for convective air currents (Fig. 2). When the hot spot is formed, burning may proceed deeper in to the dump, until the buoyancy forces are still able to support the convective currents, and along the slope, so that the whole slope area is affected by combustion.

### Prediction and Modelling

The mathematical models developed to simulate pyrite oxidation and spontaneous combustion inside the partially saturated dumps usually assume homogeneous distribution of oxidising material, as well as uniform permeability [49, 50, 61]. According to the Maardu practice, however, it has become evident that the formation of hot spots is dependent on dump heterogeneity, especially the way in which the shale is disposed.

Therefore, both homogeneous reactant distribution and uniform permeability assumptions are unsatisfactory to predict, whether, where or when the combustion takes place. The observations in Maardu detected large variations in the time scale of hot spot formation - from 4 months to 18 years [64]. The fast combustion is explained by the oxidation of a critical volume of the shale with large surface area, but also with high

permeability. The hot spots may develop inside the mound slope about 1-2 m from the surface, supported by influx of oxygen through forced convection of the blowing wind.

In contrast, the combustion occurring decades after disposal is connected with slow movement of pyrite oxidation zone towards the dump depth with subsequent slow temperature increase, until buoyancy force becomes strong enough to support free convection currents through the slope. Therefore, in order to predict the formation of hot spots, it is possible to define areas where the dump geometry is favourable, but also it is necessary to know exactly, where the shale with critical particle size was dumped and where high permeability channels are located.

### Changes in the Solid Phase

When the temperature of the waste rock gradually increases, the sequence of changes occurs. At the temperature 50-60 °C, the rate of the oxidation of organic matter increases considerably [34]. In the region 100-130 °C, physically bound water evaporates [15]. Further changes depend on oxygen supply. In the air inflow channels and other regions with good oxygen supply, the oxidation is more complete, CO<sub>2</sub>, CO and SO<sub>2</sub> being the main gaseous products and the temperature exceeds 1000 °C. In contrast, in the regions with poorer supply, a process similar to industrial semicoking develops. The oil yield is highest at temperatures 400-470 °C and the main gases are hydrocarbons, H<sub>2</sub>, H<sub>2</sub>S and CO<sub>2</sub> [16, 65].

It has been speculated that the formation of hot spots considerably increases the leaching of heavy metals out of the shale. Indeed, the experiments with shale ash, obtained as a result of artificial combustion of the pulverised shale, detected the increased rate of leaching of heavy metals (U, Mo, V) out of the shale compared with the unweathered shale [39, 40]. The possibility to extract heavy metals from the shale ash in an industrial process has been suggested [65, 66]. The study of a cooled-down hot spot in Maardu North Dump, however, indicated the layered structure of the changed material and the presence of different types of oxidation products that are different from the pulverised ash [47].

Firstly, the surface area of the dump material is orders of magnitude smaller than that of pulverised shale. Secondly, the solid phases formed in the dump are different from those in the pulverised shale ash - primarily because the industrial combustion lasts for some seconds, but the hot spot burns usually for a couple of years, as well as because the waste rock contains rock types other than shale.

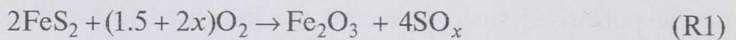
In the centre of the hot spot, the shale had changed into porous slag-type material. From the primary minerals, quartz (SiO<sub>2</sub>) and sanidine (KAlSi<sub>3</sub>O<sub>8</sub>) were still present, with illite (K<sub>0.6</sub>Mg<sub>0.25</sub>Al<sub>2.3</sub>Si<sub>3.5</sub>O<sub>10</sub>(OH)<sub>2</sub>) and pyrite (FeS<sub>2</sub>) turned into cordierite ((Mg,Fe)<sub>2</sub>Al<sub>4</sub>Si<sub>5</sub>O<sub>18</sub>), hematite

(Fe<sub>2</sub>O<sub>3</sub>) and lepidocrocite (γ-FeOOH). The colour of the slag was red (hematite present) or black (without hematite, depending on oxygen availability), in some cases covered by yellow surface layer (lepidocrocite present).

In the chemical reaction between limestone and rocks containing aluminosilicates, new minerals melilite (Ca<sub>2</sub>(Mg,Al)(Si,Al)<sub>2</sub>O<sub>7</sub>) and wollastonite (CaSiO<sub>3</sub>) had formed. The occurrence of soluble K, Mg and Ca sulphates has been detected, for example hexahydrate (MgSO<sub>4</sub> · 6H<sub>2</sub>O), picromerite (K<sub>2</sub>Mg(SO<sub>4</sub>)<sub>2</sub> · 6H<sub>2</sub>O), and ettringite (Ca<sub>6</sub>Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>(OH)<sub>12</sub> · 26H<sub>2</sub>O) [47]. The presence of ammonium sulphates has also been reported [41]. Obviously, the anhydrites have been hydrated after cool-down. According to the mineral transformations, the temperature of the hot spot was assumed to be over 1000 °C that is in accordance with the field measurements [63].

Closer to the surface, where heat exchange with atmosphere was more intensive, two different types of changed shale were found to be in abundance. In the samples of the light red type, quartz, sanidine and illite were present, but organic matter had disappeared and pyrite was oxidised into hematite. This type corresponds to the temperature region of about 500-1000 °C. The other, black type corresponds to the lower temperature region (below 500 °C) with all primary minerals present, but kerogen changed into semicoke. No leaching experiments of the hot spot material have been done.

There is, however, a large difference in the evolution of pore water pH between leaching of cooled-down hot spots and low-temperature leaching of unchanged shale. During the combustion process, shale pyrite is turned into hematite and sulphur oxides:



Thus, acidity is removed out from the dump in gaseous phase (R1). Some of the sulphur oxides react with base cations, forming sulphate minerals. Dissolution of these, however, does not contribute to the formation of acidity. Thus, the reaction of the water in connection with the hot spot material is not expected to be highly acidic. At the same time, the heavy metals U, Mo and V in the raw shale are to a large extent bound within the reduced phase (organic matter) and are not easily leachable, unless the organic matter is oxidised [47]. In the cooled-down hot spots, they occur possibly in more leachable, oxidised form. Subsequently, the high rate of heavy metal migration is expected in cases, when highly acidic water, formed during low temperature oxidation of pyrite, is transported into cooled-down hot spot area. Presently, there are no data showing how significant the contribution of this complex mechanism to heavy metal pollution is.

## Spontaneous Combustion Areas

Although the placement of the waste rock as individual mounds or disposal of the shale close to trench slopes are necessary conditions for hot spot formation, it does not mean that every mound or slope area necessarily undergoes the combustion process. As assessments of the presence of favourable conditions for spontaneous combustion, in particular permeability and critical mass, as well as the time scale of hot spot formation after disposal are connected with large uncertainties, the extent of the process has been described according to the empirical information driven from field observations.

The number of hot spots per million tonnes of disposed waste rock and per year has been used to characterise the spontaneous combustion phenomenon [67]. In 1980's, this number was 15 for the regions of random and 11 for the regions of selective disposal. After the mining activities were stopped in 1991, the number of new hot spots has been gradually decreasing and the recent survey did not detect new burning areas [47]. This is possibly due to the permeability decrease during waste rock compaction and formation of new minerals at low temperatures, clogging the pores, as well as decreased oxygen gradient because of the development of vegetation cover.

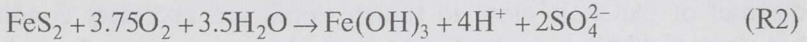
The size of individual hot spots has been variable and often limited with individual mound area, but possibly proceeding along the trench slopes. Therefore, it is very difficult to estimate the proportion of the burnt waste rock volume. The hot spots have been detected on approximately 10-15 % of the dump area, the proportion of the burnt waste rock is, however, probably much smaller.

## Low-Temperature Oxidative Leaching

Most of the dump area is not affected by the combustion, but the shale pyrite is still oxidised at a rate that is limited by oxygen transport into the dump and by the individual pyrite particles in the shale. This two-stage process produces sulphuric acid that diffuses out from the shale particles and is transported deeper into the dump by infiltrating water. The study of the weathering profile in the central part of the Maardu South Dump far from the slopes, where oxygen diffusion is the dominating transport mechanism, enabled us to develop a mathematical model MWDLM [45].

The concept of the model is analogous to the models developed to assess pyrite oxidation in acid soils, waste rock and uranium mill tailings [51-59]. As the new finding, the depth of pyrite redox zone in each individual shale lump, that appeared to be a function of its distance from the surface, was used to calibrate the model with the field data. Every square meter of the dump has, on average, a potential to generate 500 kg

of sulphuric acid in low-temperature leaching of pyrite present in the shale only. The overall reaction is



This potential is realised over a long time span, about 400-1000 years, gradually decreasing in time. These calculations do not include the pyrite, present as a several centimetres thick individual layer below the shale layer in the original overburden. The particle size of that pyrite is in the order of millimetres and the chemical rate of oxidation, expressed in moles per volume unit of the waste rock and per time unit, is several orders of magnitude lower than that of microcrystalline shale pyrite.

The main result of the modelling was that oxygen diffusion has a capability to oxidise 0.05-0.07 moles of shale pyrite per kg of infiltrating water during the first decades, changing the pH of infiltration water to between 1 and 2. The acidity is presently neutralised in reactions with surrounding rocks, mainly limestone. Thus, the presence of limestone in the overburden, that was hardly considered significant during the mine establishment, has luckily turned to be the main factor reducing the pollution problems.

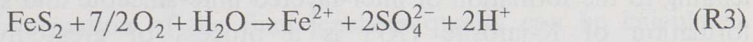
### Formation of Leachate Quality

The dump leachate is characterised by circumneutral pH (7-8.5), very high sulphate concentration (1-10 g/l) and high Mg/Ca molal ratio (1-4). The sequence of hydrochemical processes, leading to such leachate quality, includes pyrite oxidation at low temperature, formation of sulphuric acid and interaction of the acidic leachate with surrounding rocks, primarily Mg-containing limestone. Although the cooled-down hot spot areas may contribute to the local high Mg and sulphate concentrations, when salts are dissolved, their contribution is not so large that they could significantly contribute to the water quality on a regional level.

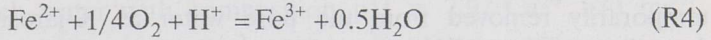
Previous studies have classified the waters into different types according to main ions, for example, separating calcium hydrocarbonate and magnesium calcium sulphate hydrocarbonate waters. Hydrochemical modelling of the oxidation and neutralisation processes coupled with phase changes made it possible to follow the main reactions that essentially take place before a final water composition is reached. The oxygen diffusion-limited pyrite oxidation rate and local partial equilibrium concept are the theoretical basis that, after coupling with field observations, allowed to illustrate the sequence. Hydrochemical modelling was carried out using computer code PHREEQC [68] and WATEQ4 thermodynamic database [69].

The main reactions are:

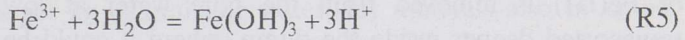
- Oxidation of pyrite inside the water saturated shale particles at pH 1-3



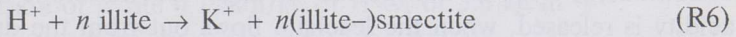
- Bacterially catalysed oxidation of Fe(II) to Fe(III)



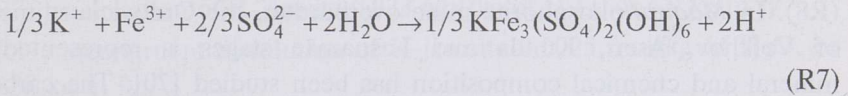
- Precipitation of amorphous ferric hydroxide at pH above 3



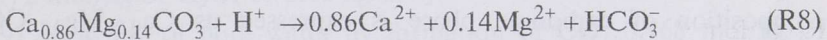
- Incongruent dissolution of illite as a K releasing mechanism



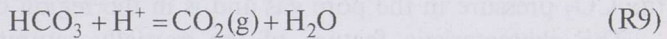
- Precipitation of K-jarosite at pH 1.5-3



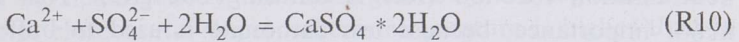
- Dissolution of Mg-containing calcite in acid solution, increasing the pH



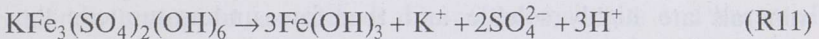
- Release of CO<sub>2</sub> into the pore gas



- Precipitation of gypsum when oversaturated



- Incongruent dissolution of K-jarosite



The combination of reactions (R3)-(R11) gives a simplified version of the evolution of the pore water quality in trenches. In practice, the hydrochemistry is much more complicated. For example, except Ca<sup>2+</sup> and SO<sub>4</sub><sup>2-</sup> ions, electroneutral complex CaSO<sub>4</sub> is present. The formation of ions and complexes different from those presented in (R3)-(R7) is also common in highly acidic waters, so the pH in that case does not express the actual acidity of the water [47].

The presence of K-jarosite, ferric oxyhydroxide and gypsum has been detected by analyses of the weathering profile samples. K-jarosite occurs as a surface layer on shale lumps. We connect the formation of K-jarosite as the result of oxidation of Fe(II) into Fe(III) by bacteria, the colonies of which are located on the surfaces of the lumps. The mechanism of K

supply for jarosite precipitation is the incongruent dissolution of illite, leading to the formation of inter-layered illite-smectite and smectite. The formation of K-jarosite (R7) is a process of great hydrochemical significance.

Firstly, some of the acidity (8 %) is buffered by  $K^+$  and some (25 %) temporarily removed from the pore water as K-jarosite. Temporarily stored acidity will be released later (R11), when microcrystalline pyrite is oxidised, changing the pH of the infiltrating water to 3-4. Secondly, most of Fe(III) is removed from the pore water at low pH, and is not transported deeper inside the dump, where it could be an active oxidant of pyrite with Fe(II) released into the pore water. Under anaerobic conditions, Fe(II) is transported through the limestone layer and the acidity is released, when the leachate flows out from the dump and is in connection with atmosphere according to R4 and R5.

Acidity is neutralised, when low pH pore water reacts with limestone (R8). In *Maardu* phosphorite mine overburden, the Ordovician limestone of Volkhov, Aseri, Kunda and Lasnamäe stages is represented, the mineral and chemical composition has been studied [70]. The carbonate phase is magnesian calcite. Accounting for thicknesses of layers and magnesium content in carbonates of different layers, the average composition of carbonate phase is expressed as  $Ca_{0.86}Mg_{0.14}CO_3$  for North Dump and  $Ca_{0.88}Mg_{0.12}CO_3$  for South Dump. The pH of the neutralised pore water (R8) in the partially saturated dump depends from the  $CO_2$  pressure in the pore gas and is in the region of 5.5-8.5.

The characteristic feature of the partially saturated and carbonate-buffered pyritic dumps is that most of inorganic carbon released in the neutralisation reaction (R8) is diffusing out (R9). This reaction is of major importance, because less carbonate is used to buffer the acidity. The neutralisation reaction is so active that most of calcium and sulphate is precipitating inside the dump as gypsum (R10). Magnesium sulphate minerals are highly soluble and therefore undersaturated; the Mg/Ca ratio in the leachate is high.

The chain of geochemical reactions (R4)-(R11) is evoked by pyrite oxidation according to (R3) and it was modelled by constructing the PHREEQC flow sheet [47]. (R3) can be considered irreversible in partially saturated dumps. Modelling (R5), and (R7)-(R10), the concept of local hydrochemical equilibrium is applicable. Inserting the value of pyrite oxidised per kg of available water, determined according to the field-calibrated diffusion model, into the hydrochemical calculations and assuming gypsum precipitation at equilibrium, the build up of high Mg/Ca ratio is in the same range, determined in leachate samples. Hence, during the first decades of the dump oxidation, about 60-80 % of sulphate released in pyrite oxidation remains inside the dump as gypsum, in accordance also with the mineralogical analysis of the weathering



profile samples. The concentration of K in the leachate is determined by the rates of (R6), (R7), and (R11).

Thus, the formation of the final leachate quality can be calculated using (R3)-(R11) in appropriate molal proportions using local thermodynamical equilibrium concept, where appropriate. For example, the typical trench water with composition pH = 7.9, Ca<sup>2+</sup> 520 mg/l, Mg<sup>2+</sup> 580 mg/l, K<sup>+</sup> 98 mg/l, SO<sub>4</sub><sup>2-</sup> 3550 mg/l, HCO<sub>3</sub><sup>-</sup> 360 mg/l, and Mg/Ca molal ratio 1.8, has hypothetical evolution (the quantities are presented in moles per kg of available water, for minerals also in kg per square meter of land surface and year, and for CO<sub>2</sub> in m<sup>3</sup> per square meter and per year):

- (R3) oxidation of pyrite 0.1 mol/kg of H<sub>2</sub>O, or 3.6 kg m<sup>-2</sup>y<sup>-1</sup>
- (R4) practically all Fe(II) oxidised into Fe(III)
- (R6) release of K<sup>+</sup> 0.033 mol/kg of H<sub>2</sub>O
- (R7) precipitation of K-jarosite 0.033 mol/kg of H<sub>2</sub>O, or 4.9 kg m<sup>-2</sup>y<sup>-1</sup>
- (R11) incongruent dissolution of K-jarosite 0.0025 mol/kg of H<sub>2</sub>O, or 0.38 kg m<sup>-2</sup>y<sup>-1</sup>
- (R8) neutralisation of acidity by dissolution of magnesian calcite 0.172 mol/kg of H<sub>2</sub>O, or 5.05 kg m<sup>-2</sup>y<sup>-1</sup>
- (R9) degassing of pore water by formation of CO<sub>2</sub> 0.168 mol/kg of H<sub>2</sub>O, or 1.13 m<sup>3</sup> m<sup>-2</sup>y<sup>-1</sup>
- (R10) precipitation of gypsum 0.14 mol/kgw, or 5.43 kg m<sup>-2</sup>y<sup>-1</sup>

### Oxidation in Temperature Region 40-100 °C

Depending on the heterogeneity and dump geometry, the regions develop inside the dumps close to the slopes, where temperature is higher than in the central parts, but does not exceed 100 °C. This temperature is often used in modelling of pyritic dumps as a boundary condition, above which pyrite oxidation is stopped, as water is one of the reactants and bacterial catalysis is not possible [49, 50].

Analyses of the lysimeter pore water sampled from the heated waste rock (50 °C) detected the pH 1.8 with U, Mo and V concentrations 15, 64 and 0.75 mg/l, respectively [72], that are about 2-3 orders of magnitude higher than in the dump leachate with circumneutral pH. As both pyrite and organic matter are oxidising in this temperature region in the presence of water, the heavy metals are released from the shale at high rate. Thus, these conditions can be most hazardous regarding water pollution and it is possible, that spontaneous combustion actually decreases the total release of the metals from the slope areas through eliminating the acidity source through emissions of sulphur oxides and binding the metals in the changed slag-like material.

## Potential Changes in Leachate Quality over Time

In future, the pyrite oxidation zone moves deeper into the dump, the concentration gradient of oxygen that is the driving force of diffusional oxygen transport decreases and so does the rate of pyrite oxidation. This should be observed primarily by decrease of sulphate content and Mg/Ca ratio in the leachate. There is, however, the lower limit of sulphate concentration, corresponding to the gypsum equilibrium. The decrease of sulphate concentration below 1200 mg/l is expected, when gypsum, presently accumulating in the dump, has dissolved. This will happen after several hundreds of years only.

The more arguable question remains, whether the available buffering capacity of limestone will be locally and regionally depleted before all available pyrite is oxidised. Limestone is an excellent natural buffer of the acidic drainage and the amount of limestone present on the dump is in excess to buffer all acidity by the factor of about 4-5. This type of acid-base accounting approach, however, is a poor assumption in the Maardu case, where the limestone has been disposed mainly as big lumps.

The study of the weathering profile in Maardu showed that calcite concentration in the small fraction (<1 mm) is very small and is rapidly depleted in interaction with the acidic drainage. The acid product K-jarosite has been accumulating in the same fraction. The big limestone lumps appeared to be armoured by new precipitates, mainly gypsum and ferric oxyhydroxides, but some lumps also by a second layer of K-jarosite. Subsequently, the central parts of the lumps have been excluded from the neutralisation reaction.

Two areas of the site are of primary concern. At the northern boundary of the site, the limestone layer was very thin and the calcite/pyrite ratio the smallest. Forming the dumps of the eastern part of the North Dump, the selective disposal technology was used and most of the limestone was disposed above the shale layer. The rate of the acidity production per kg of infiltrating water has been calculated for this case to be about 1-2 orders of magnitude higher than the alkalinity, dissolved in the infiltrating water in connection with limestone.

Thus, the limestone disposed above the shale layer is practically excluded from the buffering reaction. In Maardu South Dump, where also selective disposal was used, the water table has recently risen and the shale layer is presently located below the water table, decreasing the pyrite oxidation rate in this layer by several orders of magnitude.

Presently, the field data available for Maardu dumps are insufficient to predict if the Maardu dumps may act as a geochemical time bomb. The potential decrease in the availability of limestone buffering capacity is followed by sharp decrease in pH and possible increase in concentrations of Al (at pH 3-4.5) and Fe(III) (at pH below 3), as well as the heavy metals. The sudden acid discharge possibly occurs after heavy rainfalls or

in the spring after snowmelt. The key to understand, whether or when this might happen, is to study the development of limestone depletion and armouring zones deeper inside the dump, and especially in critical areas.

## Environmental Quality of Maardu Dumps and Surroundings

During the last years, 5-7 years after mining activities were stopped, no new hot spots have been observed to be formed. In North Dump, the rapid combustion of waste rock in favourable conditions, compaction of the waste rock in time, formation of new precipitates that clog the pores and development of vegetation cover are some of the reasons. In South Dump, the risen water table excludes the possibility of spontaneous combustion in the areas, where selective disposal method was used. Regarding possible developments, however, any operations that involve redisposal of large waste rock volumes may cause rapid combustion.

The low-temperature oxidation of pyrite will continue for hundreds of years and can be assessed according to the Mg/Ca ratio in the leachate. The possibility of sudden discharges of acid and heavy metal-rich water is unclear and needs further studies. The sulphate-rich leachate from the site pollutes regional ground water, as well as Lake Maardu and Kroodi River. Even if the leachate is diluted by the factor of 10, the sulphate content is still high and above the highest permissible concentrations for potable water and fisheries. Until 1991, the leachate was directly pumped to Lake Maardu and Kroodi River. Now, the impact of the leachate to the deterioration of the regional ground water quality has possibly increased.

The assessment of the quality of vegetation cover formed on the dump surface is controversial. It has been found that the soil developed during the weathering of limestone and shale mixture best supports the vegetation growth [73]. Obviously, the shale supplies the soil with nutrients, such as K and Mg, whereas limestone guarantees the neutral reaction of the soil water. It has also been detected, however, that the concentrations of a range of heavy metals (Cr, Mn, Ni, Pb, Zn, Mo, Co) in plants developed on such soils is higher by a factor of 2-25 than in surrounding areas [36].

The soil formed from the shale as a single source rock is acid and the vegetation growth in the areas, where the shale was disposed directly on the surface, is hindered. The concentrations of As up to 100 ppm have been found in such soils, and the concentrations of U, Mo and V are close to those in the unweathered shale (40-60, 200-400 and 300-800 ppm, respectively). In some samples, collected from the cover layers formed on limestone and shale lumps, anomalously high concentrations

of Cd (up to 200 ppm) have been determined [71]. It is unclear, whether or for how long the vegetation cover has the rehabilitative character, or when, if ever, the over 10 km<sup>2</sup> area could be used for agricultural or recreational purposes.

## Maardu Experience and Potential Phosphorite Mining in Estonia

In the areas of other Estonian phosphorite deposits, that could be mined using open cast methods (Toolse, Aseri, Vihula, Viru-Nigula), the shale layer lies directly above the phosphatic sandstone layer and is covered by glauconite sandstone and limestone. Thus, if the shale is not commercially used, it has to be disposed and needs special attention because of its capability to combust spontaneously and the content of pyrite and heavy metals. The feasibility studies of exploiting these phosphorite reserves have to include the excessive costs rising due to shale handling.

The discussions, if the shale should be approached as a potential industrial raw material, have been held in Estonia over the last decades. The technologies of combusting the shale industrially in fluidised bed and extracting heavy metals from the shale ash have been developed in Estonia [65, 66, 74]. Eventually, however, the content of both organic matter and heavy metals in the shale is too low for industrial use with better quality fossil fuels and metal ores presently available in the world market. In addition, the residues formed during the shale combustion and metal extraction are more hazardous than the raw shale.

The ash content of the shale is 80-90 % and the release rate of heavy metals from the pulverised shale ash high because of the large surface area. If some of the metals are extracted in acid leaching, large volumes of used acid are the by-product and other metals still remain in the residue. Any industrial complex established for the shale combustion or processing will produce large quantities of hazardous waste and the technology of environmentally safe disposal of that waste is even more complicated and expensive than that of the raw shale.

The reactivity of the shale, expressing the amount of oxygen adsorbed by the shale during a time unit at a certain temperature, has been found to be 2-5 times higher in other deposits, and the content of pyrite also 2-2.5 times higher [34]. The Maardu experience showed, that the rocks present in the overburden were too porous and permeable after excavating to guarantee a sufficient barrier against oxygen influx, even if the shale was disposed selectively.

The 1-2 m thick layer of limestone lumps may turn out to be covered by gypsum and Fe-containing precipitates and, therefore, not sufficient to buffer the acidity formed during pyrite oxidation. In addition, this

layer may serve as a low permeability channel for convective air currents, if the trenches surrounding the waste rock plateaus remain dry. By these means, the understanding of the dump processes in late 1980's both in Estonia and by Soviet Nutrient Industry Ministry officials was so poor, that the national protest against new mine developments was fully justified.

If the Estonian phosphorite ore turns out to be commercially feasible and environmentally acceptable to be mined, but the shale not, the only option is the rapid redispersion of the shale into anaerobic conditions. Various options have been worked out to construct barriers against oxygen diffusion into the dump, including establishment of clay or moraine barrier [42] and water saturated capillary barrier [75] below the topsoil layer.

Another option is direct disposal of excavated shale below the ground water table or in the bottom of an artificial water body. If the waste rock has been already oxidising under partial saturation conditions for a number of years, the option that involves the disposal of organic-rich layer, such as sewage sludge with high oxygen consumption reactivity, on the dump surface in order to reduce oxygen concentration gradient, may lead to undesirable reduction of newly formed minerals with release of heavy metals [76].

The possibility of the potential use of the disposed shale in the long term should also be considered in the planning process. It is evident, however, that the disposal site cannot be constructed using the overburden material only. Even if the particle size of limestone is considerably decreased by grinding that increases the surface area and guarantees neutralisation of the acidity, the sulphate pollution is still inevitable. Thus, local external source materials for the disposal site development, such as Cambrian clays, should be investigated, but that option may turn out to be far too expensive and make mining unfeasible.

## Summary

The careless disposal of the shale in Maardu dumps led to the spontaneous combustion of the waste rock and different negative environmental impacts – air pollution and destruction of newly formed vegetation due to mine fires, and regional water pollution because of low temperature oxidation of shale pyrite that presently is realised as high sulphate contents in ground and surface water fed by the dump, but in longer term may lead to local and regional pollution with toxic metals.

The hydrochemical calculations proved that temperature rise and spontaneous combustion is not the main cause of regional high sulphate loads, as has been thought previously. Low-temperature oxidation of the

shale dictates the regional water quality and can be expressed as a sequence of multiphase reactions, started by irreversible pyrite oxidation reaction and ending with leachate that contains sulphate and hydrocarbonate as main anions and  $Mg^{2+}$ ,  $Ca^{2+}$  and  $K^{+}$  as cations. The oxidation of pyrite in low temperature areas is rate limited by two-stage diffusional transport of oxygen to the micron-sized pyrite grains - first in gaseous phase through partially saturated large dump pores and channels, and then dissolved in water through shale micron-sized pores. The amount of pyrite oxidised as a function of depth can be calculated using the computer code, specially written for Maardu case.

The heterogeneity in the dumped material positioning and particle size distribution, as well as armouring of the waste rock lumps by new precipitates increases uncertainty in assessment of the potential decrease of the readily available buffering capacity in time. The current age of the dumped material between 7 and 34 years means, that the dump is still in the early stage of the active oxidation phase that lasts for hundreds of years. Hence, monitoring of the dump leachate quality and neutralisation front movements is necessary, especially in the areas, where the thickness of the limestone layer in the overburden before mining was small, and where the shale has been disposed selectively with shale lumps layer positioned above the ground water table.

Simple and well-known methods are available in order to avoid spontaneous combustion, the main objective of which is not to dispose the shale close to the slope areas with high permeability. The study of the Maardu dumps, however, demonstrated that low-temperature oxidation is undesirable from the point of acidity generation, water pollution and potential bioaccumulation effects and should be minimised by guaranteeing anaerobic conditions inside the shale disposal site.

This technology is much more complicated and expensive, and involves using of materials other than those available in the overburden. The Maardu example belongs to the period when the relevance of the shale oxidation to the environment quality was poorly understood by the mining company, and the importance of the environment quality, too, was undervalued. The development of a selective disposal technology in early 1980's that did not avoid the formation of hot spots, and even increased the potential of breakthrough of acid water, demonstrates that the nature, complexity and importance of different transport processes has to be better understood.

Several questions remain unclear and should be addressed in further studies, including

- (1) The accumulation of heavy metals (Cd, U, Mo, V) at redox and pH fronts and bioaccumulation in plants

- (2) The rate of leaching of heavy metals out from the different types of heated material and the extent of the transport of acid water into cooled-down hot spots
- (3) Depletion of the availability of the buffering capacity of limestone in deeper layers of the dump
- (4) Rates and mechanisms of the low-temperature oxidation of the shale organic matter

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