ARTU ÜLIKOOLI
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TARTU 1994

GEOCHEMICAL ZONATION OF MAARDU MINE TAILINGS DUMP

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Introduction

Opencast mining of phosphorite in Maardu pit near Tallinn has lead to pollution of surrounding hydrosphere due to inaccurate disposal of Dictyonema shale, layer of which was a part of the overburden of phosphorite layer (Naumov, 1991). Total area of disposal site is about 10 sq km, thickness of disposed rocks and sediments 12–18 m, and slope angle of the edges 30–40 degrees. Dictyonema shale contains pyrite (average 4–6%), organic matter (15%) and anomalously high concentrations of a range of heavy metals (V 800 ppm, Mo 130 ppm, U 50 ppm; Pukkonen, 1989; Maremäe, 1988); main rock-forming minerals are quartz, illite and orthoclase (Palvadre et al., 1984).

High porosity and permeability of disposed rocks and sediments favours oxidation of fine-grained shale pyrite, followed by release of sulphur and heavy metals from the shale. Sulphates and heavy metals are distinguished as main pollutants, leached out from the site and entering ground water, lake Maardu and the Baltic Sea (via Kroodi gully). Analyses, however, have shown, that major part of a range of heavy metals (V, Mo, U, Cu etc.), released from the shale, is not entering watercourses according to the release rate, i.e. is adsorbed and/or precipitated within the dump. This occurs mainly because of large amounts of limestone in the dump, what buffers the acidity produced by pyrite oxidation and natural acidity of infiltrating water. Long-term performance of the dump should therefore be of serious concern because of possible depletion of buffering capacity. Due to heterogeneity of dumped material and different physico-chemical processes, regions with different characteristic mineral associations are formed within the site both in vertical and horizontal dimension. Recognition of these regions assists to find areas which may serve as geochemical barriers for different pollutants.

The aim of this study was to distinguish these regions on the light of governing physico-chemical processes together with discussion from the point of possible accumulation of pollutants according to obtained field-data. Kinetic information about these governing processes should assist to make long-term predictions in future.

Materials and methods

Approximate lithological composition of disposed rocks and sediments in Maardu South Pit dump is assessed to be: Dictyonema shale 37%, limestone 26%, glauconite sandstone 10%, quartz sandstone 18%, quaternary sediments 8%, pyrite and pyrite sandstone 1% (Naumov, 1991). Approximate mineral content calculated according to this composition appears to be: calcite 21%, dolomite 2%, quartz 33%, feldspars 11%, clay minerals 16%, pyrite 3%, glauconite 7%, organic matter 6%.

Great variations in particle sizes of dumped rock and sediment types, and consequently in particle size distributions occur throughout the site. When sandstones and quaternary sediments have quite uniform particle size distribution (dominating fraction 0.05–0.5 mm), that of limestone and Dictyonema shale varies from clay fraction to big lumps. Mine tailings were dumped on the areas of worked-out Maardu North and Maardu South pit for almost 40 years (1955–1992). Presumably, oxidation of shale pyrite in earlier dumped areas has developed further inside the dump. In addition, approximately 10% of the area has suffered under self-ignition, especially near the edges of the dump and in case of unevenness of the surface.

In order to get insight in both fast (years and tens of years) and slow (hundreds and thousands of years) developing processes, as well as to compare areas, where self-ignition has and has not been followed (self-ignition areas are easily detected by gas emissions, risen surface temperature and consequent lack of snow cover in winter), detailed survey area was chosen in Maardu South Pit. Approximate boundary between burnt and unburnt area was fixed by records of Dr. Naumov (Institute of Geology, Estonian Academy of Sciences). Tailings samples from this area were taken by author in summer 1993. Core drilling at two locations (both dumped 10 years ago, but of different distance from the edge — 10 and 200 m) was carried out by EKE EMV and core sampled in the field by author. Samples were also taken from the levelled-up surface and from the slope of the dump. Altogether, 30 tailings samples were taken, pulverized and scanned on X-Ray diffractometers DRON. Powder diffraction patterns were compared with JCPDS files and catalogues of Tartu University Mineralogy Laboratory. In addition, 3 samples were analyzed by differential thermal analysis using Derivatograph.

Heterogeneity of the dump, as well as heterogeneity of drilling core material made questionable representativeness of core sampling. To overcome this problem, material with grain size <1mm was comparatively analyzed from both drilling cores at different depth intervals, assuming that a large part of this fraction originates from decomposition of the shale. This assumption was controlled by determination of concentrations of other minerals (quartz, illite, orthoclase) which occur in the shale in characteristic ratios. Shale particles and new-formed minerals from different depths were analyzed separately.

Representative sampling of surface layers and the slope of the dump was also complicated due to visible heterogeneity of the material. Dictyonema shale and soil samples were taken from different locations on the surface. Visually fixed new-formed minerals from the cover layer of the shale lumps were analyzed. Samples taken from the slope represented clayey material of different colour (yellow, white, green), formed in the process of weathering of the shale and other rocks.

Except X-Ray powder diffraction analysis, all samples were semi-quantitatively analyzed for wide range of elements (Si, Al, Fe, Mg, Ca, Sc, Ti, V, Cr, Mn, Co, Ni, Cu, Pb, Zn, Mo, Ag, Sn, Li, B, Be, Sr, Ba, P, U, Zr, Nb, La, Ce, Gd, Dy, Ho, Er, Yb, Y, Ga, Ge, As, Tl, W) using plasma emission spectroscopy in the Laboratory of Geological Survey of Estonia. This was done in order to make preliminary assumptions about possible anomalies. From these elements, Fe, V, Co, Ni, Cu, Zn, Mo, P and U were chosen to be further discussed on the basis that

(i) concentration of element may produce environmental hazard, and/or

(ii) concentration of element in particular location in the dump cannot be explained by heterogeneity only (i.e. accumulation is taking place).

All the data were overlooked from theoretical approach discussing governing physico-chemical processes and their possible impacts in both short- and long-term.

Results

Summarized results of drilling core and soil samples analyses are given in Table. These data are used to discuss possible redistributions of pollutants within the site, and their migration into watercourses.

Drilling cores (samples 1–21 in Table).

Minerals. Pyrite (FeS_2), gypsum ($CaSO_4 \cdot 2H_2O$) and anhydrite ($CaSO_4$) were used as indicators of processes. Anhydrite was found in the region of supposed hot spot only (see samples 13, 14, 20, 21 in Table). Semi-quantitative analysis methods enabled to determine percentage of these minerals in each sample. Approximate assessment of pyrite oxidation was done by quantitative comparison of pyritic iron content with total iron in the sample. These results are presented on Figure 1. Other determined minerals were quartz, illite, feldspars, glauconite, apatite, chlorite, and calcite.

Elements. After 10 years of changes, V, Mo and U do not tend to concentrate in higher concentrations than those in original shale. Concentrations of Fe in observed hot spot are higher than in upper layers. Below hot spot, in dolomite- and calcite-rich layers, Co, Ni and Zn are observed to be concentrating (see sample 14 in Table). The same phenomena is followed in sulphate covers of limestone lumps in the hot spot area (see sample 21).

Surface, slope and near-by ditch of the dump.

On the levelled-up surface of the dump, water is leaching elements from the shale into the dump. Jarosite is observed to be formed in a cover layer of shale lumps with considerable amounts of V and Mo carried into the dump (see samples 22 and 23 in Table). On overall scale, however, importance of this phenomena is insignificant. On the slope of the dump, surface runoff and exit of water from inside the dump are also important. This allows formation of new minerals, especially jarosite, gypsum, smectite and amorphous ferric hydroxide. Presence of ferric hydroxide was determined in samples 24–26 by differential thermal analyses. Concentrations of other metals except iron in these sediments are not significantly higher than those in original Dictyonema shale. In the peat of near-by ditch, Zn and P tend to concentrate (see sample 27 in Table).

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
	Location	Type	Depth,m	Fe, %	V, ppm	Co, ppm	Ni, ppm	Cu, ppm	Zn, ppm	Mo, ppm	P, ppm	U, ppm	Main minerals	Py %	Gy %	Anh %	Py/Fe
1	DC 1	fr <1mm	1,1	4,8	600	10	60	100	100	200	1000	40	Q,Or,III,Gy	1,6	12,4	0	0,3
2	DC 1	fr <1mm	1,8	4,9	600	6	60	80	120	100	nd	nd	Q,Or,III Gy	2,5	7,9	0	0,5
3	DC 1	fr <1mm	2,4	1,4	600	3	25	30	60	80	nd	nd	Q,Or;III,Gy	2,2	5	0	1,6
4	DC 1	fr <1mm	3,1	2,8	300	6	40	60	80	60	2000	nd	Q,Or,III,Gy	3,2	20	0	1,1
5	DC 1	fr <1mm	6	2,1	200	9	50	80	40	30	6000	nd	Q,Or,III,Py	4,4	0	0	2,1
6	DC 1	fr <1mm	8,2	2,6	150	9	40	80	100	30	8000	nd	Q,Or.III,Py,Ap	5,7	0	0	2,2
7	DC 1	Dict shale	0,9	2,8	400	6	60	150	150	300	nd	40	Q,Or,III	2,9	0	0	1,0
8	DC 1	Dict shale	1,8	2,1	600	8	80	60	600	80	nd	nd	Q,Or,III,Py	4,5	0	0	2,1
9	DC 1	Dict shale	2,4	3,5	600	8	80	100	100	150	nd	nd	Q,Or,III	3	2,7	0	0,9
10	DC 1	Dict shale	3,1	2,1	400	8	80	100	100	80	nd	nd	Q,Or,III	4,3	0	0	2,0
11	DC 2	fr <1mm	2,5	3,5	600	10	70	100	200	35	nd	nd	Q,Or,III	3,9	0	0	1,1
12	DC 2	fr <1mm	5,7	5,6	400	10	80	100	300	100	300	nd	Q,Or,III	4,5	4,9	0	0,8
13	DC 2	fr <1mm	7,2	10,5	200	15	60	50	150	30	600	nd	Q,Or,III,Anh	0	4,1	9,6	0,0
14	DC 2	fr <1mm	9,1	5,5	300	40	200	60	1500	40	2000	nd	Do,Ka,III,Gl	0	0	5,8	0,0
15	DC 2	fr <1mm	11	4,2	200	7	60	80	150	40	10000	nd	Q,III,Or,Py	7,2	2,1	0	1,7
16	DC 2	fr <1mm	12,7	2,8	200	8	60	80	200	40	4000	40	Q,III,Or	3	4,7	0	1,1
17	DC 2	fr <1mm	14	2,9	100	6	25	25	70	7	3000	nd	Q,Ka,Do,Or,Gl	0	0	0	0,0
18	DC 2	Dict shale	2,5	2,8	600	13	100	100	250	60	nd	40	Q,Or,III	4,6	0	0	1,6
19	DC 2	Dict shale	5,7	2,6	1000	10	90	130	250	150	nd	60	Q,Or,III	4,2	0	0	1,6
20	DC 2	Dict shale	7,2	5,6	500	8	60	100	100	60	nd	40	Q.Or,III	2,6	6,1	3,2	0,5
21	DC 2	Gy cover	7,2	10,5	250	40	300	20	2000	8	3000	nd	Gy,Anh,Q,III	0	28	14	0,0
22	Surface	Dict shale	0	2,8	800	4	40	30	40	100	nd	nd	Q,Or,III,Jar	0	0	0	0,0
23	Surface	Dict sh cover	0	2,7	300	3	20	40	30	60	nd	nd	Q,Or,III,Jar	0	0,8	0	0,0
24	Slope	yellow clay	0	5,5	250	7	40	40	200	250	nd	40	Q,Jar,Gy,Sm,III	0	20	0	0,0
25	Slope	Gy cover	0	10,4	150	10	40	60	300	40	2000	nd	Gy,Q,III,Jar	0	35	0	0,0
26	Slope	brown cover	0	14	100	10	40	70	200	25	6000	nd	Gy,III,Q	0	30	0	0,0
27	Ditch	peat	0	1,1	10	10	20	80	1000	10	40000	nd	Ka,Q	0	0	0	0,0
	DETECTION	LIMIT		0,1	3	3	1	1	10	1	300	40		1	0,8	2	

Table 1. Selected data of solid phase analyses. Minerals: Q-quartz, Or-orthoclase, Ill-illite, Py-pyrite, Gy-gypsum, Ap-apatite, Jar-jarosite, Sm-smectite, Ka-calcite, Do-dolomite, Gl-glauconite. DC1-drilling core 1 (in the middle part), DC2-drilling core 2 (near the slope).

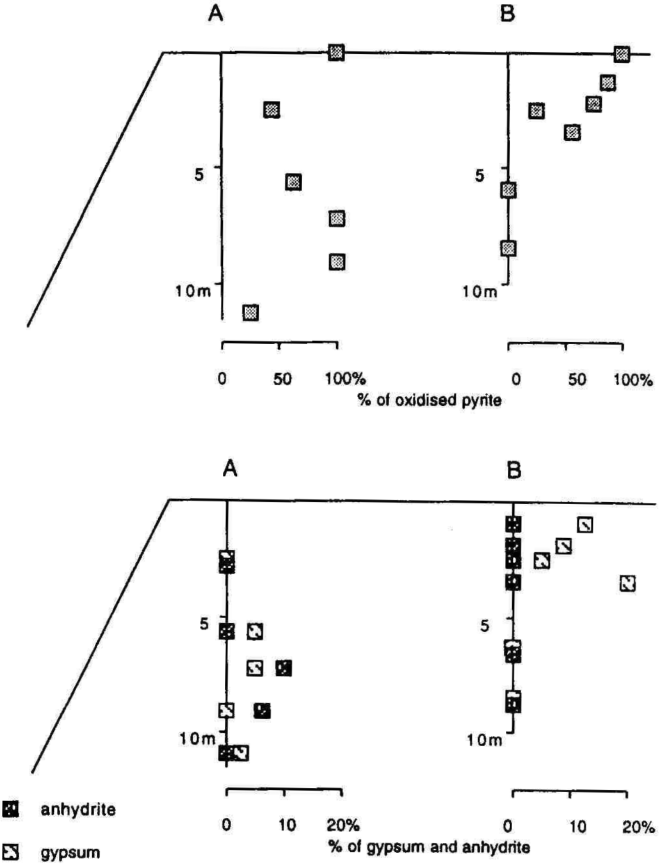

Fig. 1. Schematic diagram of pyrite oxidation and content of calcium sulphates in drilling core materials from near the edge (A) and in the middle (B) of the dump.

Governing physico-chemical processes

Oxidation

The fine-grained character of the shales (1–10μ) determines, that rate limiting factor of pyrite oxidation should be either reaction kinetics, micropore diffusion in shale particles, or macroscopic transport of oxygen by diffusion and convection into the dump. On the surface and upper layers of the dump, kinetics and diffusion of oxygen through shale particle pores are rate limiting, domination of one or another depends from shale particle size. Inside the dump, macroscopic transport of oxygen through porous media of the dump appears to be rate limiting. In middle parts of the site (over several tens of meters from the edge), oxidation of pyrite is controlled by oxygen diffusion, accompanied by moderate temperature rises (20–30°C) inside the dump. Near the edges of the dump, however, convective air currents cause self-ignition of disposed material with temperature rises over 200°C. Schematic diagram of the dump showing governing processes in three different zones is presented on Fig.. 2.

Zone 1: Surface and upper layers of the dump. Reaction rate of pyrite oxidation is limited by reaction kinetics or oxygen diffusion in shale particles. On the surface, characteristic time scale of shale pyrite oxidation ranges from several months to several years. Bacterial activity and climatic conditions are most important.

Zone 2: Deeper layers in the middle of the dump. Reaction rate of pyrite oxidation is limited by oxygen diffusion through porous media. Reaction front is moving towards the depth, but this front is not sharp. Oxygen transport is a two-stage process, diffusion through the pore space of the dump followed by diffusion into reaction sites within the shale particles comprising the dump, second stage however contributes insignificantly to characteristic time scale of oxidizing all shale pyrite in Maardu (several hundreds of years). Temperature is risen due to heat released in pyrite oxidation for about 20–30°C.

Zone 3: Deeper layers near the edges of the dump. Diffusion-caused temperature rise induces convective air currents, which are going to dominate in oxygen transport within this zone, if permeability is high (in order of 10^{-9}–10^{-10} m^2). When temperature is risen up to 60–70°C, organic matter starts actively participate in oxidation reaction, leading to self-ignition with temperature rises of hundreds of degrees. Characteristic time scale of 'hot spot' formation in Maardu is few years, however it may range from several months to tens of years (Pihlak, 1986). Location and size of each 'hot spot' depends from configuration of the dump edge and heterogeneity of disposed material. In Maardu case self-ignition is often followed along all continuity of the edge. Front between this and other zones is sharp, with transition layers.

Reactions

At low temperatures, overall reaction of pyrite oxidation in Maardu may be expressed as
$FeS_2 + 15/4\ O_2 + 7/2\ H_2O + 4\ H^+ + 2\ SO_4^{2-}$ (1).

This reaction is catalyzed by bacteria *Thiobacillus ferrooxidans* or *Thiobacillus thiooxidans*. Acidity produced in reaction (1) is neutralized by calcite, the main mineral in limestone from overburden, disposed mixed with the shale; at low temperatures, gypsum is produced:
$H_2O + CaCO_3 + H_2SO_4 = CaSO_4 \cdot 2H_2O + CO_2\ (g)$ (2).

Reactions (1) and (2) contribute to temperature rises in zones 1 and 2, and to initial temperature rise in zone 3. In hot spots, overall reaction of pyrite oxidation and anhydrite formation may be expressed as
$FeS_2 + (6+x/2)\ O_2 + 2\ CaCO_3 = 2\ CaSO_4 + 2\ CO_2 + FeO_x$ (3),
where x is 1, 4/3 or 3/2 depending from availability of oxygen, with wuestite (FeO), magnetite (Fe_3O_4) or hematite (Fe_2O_3) formed, respectively. If temperature in hot spot exceeds 800–900°C, calcite decomposes:
$CaCO_3 = CaO + CO_2$ (4).

When hot spot is cooled down, CaO and $CaSO_4$ react with water, with portlandite ($Ca(OH)_2$) and gypsum formed:
$CaO + H_2O = Ca(OH)_2$ (5);
$CaSO_4 + 2\ H_2O = CaSO_4 \cdot 2H_2O$ (6).

Reaction (6) may have temporary stage with $CaSO_4 \cdot 0.5H_2O$ formed.

Overall complex of reactions, especially range of those occurring in hot spots at different temperatures, is much more complicated, as shown for example in Veski et al., 1990. Analyze of presence of minerals, formed according to reactions (1)–(6), however, allows to make simplified assumptions about processes, taking place inside the dump. New-formed calcium and iron minerals are used as indicators to describe these processes.

Leaching

The leaching of a wide range of metals depends on the oxidation of largely insoluble metal sulphides to the much more soluble sulphates. Best practice of alum shale handling has shown, that engineered barriers for the prevention of weathering reduce leaching rates of metals such as Fe, Cu and Ni by several orders of magnitude (Allard et al., 1991). Experiments carried out to determine leaching rates of metals from Dictyonema shale ash show considerable rise in leaching rates of U and V in comparison with unburnt shale (Palvadre, Kleemeier, 1982). Leaching rates are higher also from unburnt shale at risen temperatures (Palvadre et al., 1990). Hence hot spot areas appear to be significantly increasing pollution load from the dump in short term. Reactions (2) and (3) however define buffering capacity inside Maardu dump. The pH of leachate from the site has been recorded to range from 7.4–8.3 (Naumov, 1991). According to approximate calculations, 1 000 000 kg of SO_4^{2-}, 300 000 kg of Ca^{2+}, 150 000 kg of Mg^{2+} and 500 kg $Fe^{2+,3+}$ is leached out from 1 sq km of the pit per year (Naumov, 1991). Assuming that most of sulphur and iron originates from pyrite, mobility (here defined as amount of element in pyrite carried out from the site per unit of time) of S in form of SO_4^{2-} is somewhat 600 times higher than mobility of $Fe^{2+,3+}$. Iron and supposedly a range of other metals released from the shale after pyrite oxidation (including some potentially hazardous ones) remain in large extent trapped inside the dump through precipitation and adsorption. Mass balance according to reactions (1) and (2) interpolated on all waste rock material shows excess of calcite for about 3–6 times (for different sites) in order to neutralize all acidity produced by pyrite oxidation. Limestone, however, is dumped mainly as big lumps, cover layer of which only participates in these reactions. This is a subject of serious concern regarding to dump performance in long term. When rates of pyrite oxidation and acidity generation are relatively easily predictable, assessment of buffering capacity and the rate of its depletion appears to be complicated, and most significant regarding to the dump performance.

Discussion

Based on theoretical approach and analyses of samples from Maardu site, summarized prediction of accumulation and leaching of elements, ions, or complexes is given on Fig. 3.

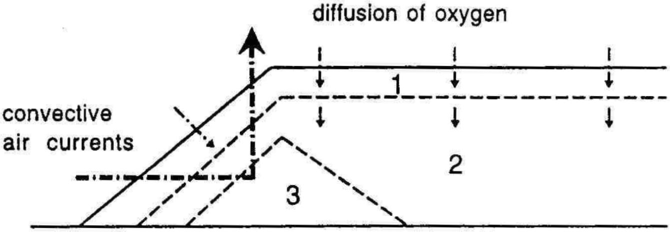

Fig. 2. Schematic diagram of Maardu dump zonation depending on character of oxidation.
Zone 1: surface and upper layers, zone 2: deeper layers in the middle, zone 3: deeper layers near the edges.

In long term, overall performance of Maardu dump is mainly affected by processes inside the dump in the middle areas (see zone 2 on Fig. 2), as contaminants from upper layers will be leached downwards by infiltrating water. Main phenomena to account for in consideration of possible barriers for pollutants in this zone are:

(1) Slowly downwards moving redox front (according to preliminary assumptions, 5 cm/yr as average; see (1) on Fig. 3);

(2) Sharp pH front mainly depending on location and particle size of disposed limestone (Fig. 3, (2));

(3) Increasing towards depth (until redox front, where exothermal reactions occur) temperature of disposed tailings (gradient in order of 3–10°C per m with maximum temperature rise of 30°C);

(4) Slowly decreasing towards depth temperature beneath the redox front, and decreasing temperature of the groundwater when moving to surroundings;

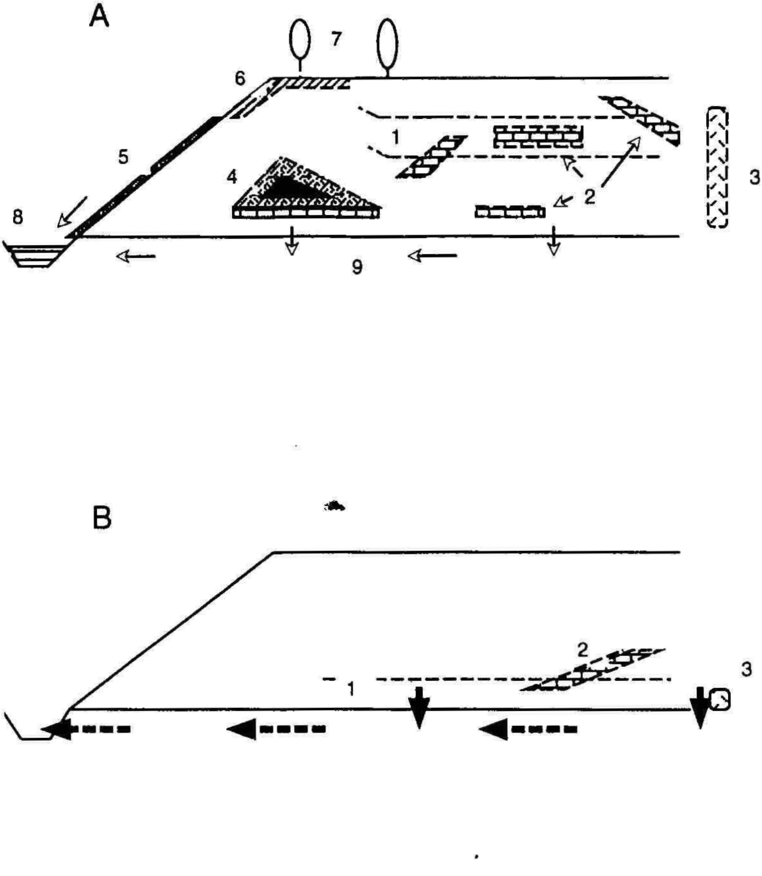

Fig. 3. Short-term (A; during tens of years) and long-term (B; hundreds and thousands of years) accumulation and migration of possible contaminants in Maardu.

1 – redox front inside the dump; 2 – buffering capacity of limestone, 3 – adsorption capacity, 4 – self-ignition hot spot; 5 – redox front on the slope; 6 – precipitation from hot gases; 7 – bioaccumulation in plants; 8 – accumulation in near-by ditch; 9 – migration.

(5) Adsorption capacity of different types of disposed materials, in most cases a function also of pH and redox potential (Fig. 3, (3)).

Other main items to discuss are bacterial activity, heterogeneity of the dump, possible channeling in contaminant transport, and seasonal variations in oxygen supply (for pyrite oxidation) and water supply (for contaminant transport). However, assuming, that accumulation of particular contaminant is favoured by any of listed above mechanisms or their interaction (through precipitation, coprecipitation or adsorption), rates of release of these contaminants into groundwater and surface water bodies should be expected to increase after certain time period, when breakthrough occurs. Hence calculations to predict time scale of leaching out certain contaminant according to presently measured concentrations (Naumov, 1991) could be misleading. Long term behaviour of the dump has to be assessed in complex way with special attention to possible depletion of pH buffering capacity and adsorption capacity inside the dump. Decrease of pH leads inevitably to dissolution and desorption of accumulated elements (see Fig. 3, b). Assessment has to be carried out, how seriously Maardu dump should be considered as 'geochemical time bomb'.

In short term, surface runoff from slopes and leachate originating from cooled-down hot spots (see Fig. 3, (4)) are significantly contributing into pollution load from the site. Places on the slope were waters from the dump are reaching the surface should be surveyed for redox barriers (Fig. 3, (5)). In deeper layers near the edges of the dump, where hot spots occur (zone 3 on Fig. 2 and (4) on Fig. 3), wide range of different reactions takes place. Important is to assess thermal decomposition of Dictyonema shale organic matter in anaerobic conditions, which produces liquid and gaseous organic contaminants. Hot gases emitted during burning are impeding both infiltration and pyrite oxidation in upper layers. Hence concentration of pyrite in upper layers near the edges of the dump may be even higher than that in the middle of the site (see Fig. 1). Precipitation of elements from hot gases is also possible (Fig. 3, (6)). On the surface of the site, plants uptake certain range of elements (Fig. 3, (7)), what is also important to analyze because of possible land use problems. Some ions however (Ca^{2+}, Mg^{2+}, SO_4^{2-}) tend to migrate into surface water bodies and groundwater (Fig. 3, (9)). Tendency of peat in near-by ditch to adsorb pollutants (Zn, P) needs also to be followed (Fig. 3, (8)).

Geochemical zonation

Majority of studies of metal pollution from waste dumps and mining sites have focussed on division of metals, ions and complexes according to decreasing mobility, determined from leachate samples and overall dump mass balance. Based on these data, time scale of leaching out of particular contaminant may be calculated. In particular cases, these calculations make misleading and even dangerous assumptions about performance of the dump in long term. Much less data is available about actual processes and developing fronts inside the dump. Because of heterogeneity and variety of disposed materials, it is economically unfeasible to carry out representative sampling on the site, as well as to include all data in calculations using geochemical codes. There are some processes however which can be quite easily described and rate of which is possible to calculate, as for example pyrite oxidation reaction controlled by macroscopic oxygen transport mechanisms in Maardu case. Using theoretical approach, geochemical zonation of a dump may be carried out, getting overview of main processes, reactions and developing fronts. Then, more or less representative sampling of the site may be done. On the basis of theoretical information bound with actual empirical representative data from the site, predictions can be given.

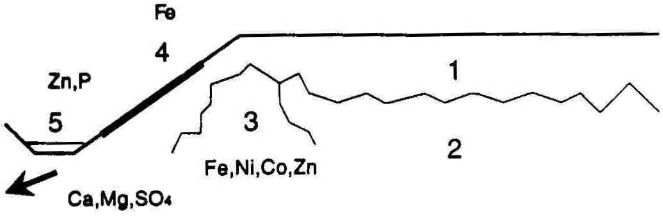

Fig. 4. Geochemical zonation of Maardu dump with elements accumulating in these zones in short-term.

1 – upper layer, 2 – bottom layer; 3 – self-ignition areas; 4 – slopes; 5 – ditches.

Available data and theoretical considerations allow to divide Maardu dumps into following geochemical zones (see Fig. 4):

1. Upper layer of the dump. Aerobic conditions. Shale pyrite oxidized, iron hydroxide and sulphuric acid produced. In case of availability of reactive limestone, gypsum is precipitated and heavy metals coprecipitated and/or adsorbed. Lack of limestone and depletion of its buffering capacity followed by leaching of metals towards depth. Heterogeneity of the dump depends on distribution and particle size of dumped limestone and distribution of Dictyonema shale, complicating the predictions. Zone develops towards depth with decreasing velocity, supposedly reaching bottom layers in 200–300 years. Bacterial activity determines the kinetics of pyrite oxidation. Surface temperature is 10–20°C higher than average atmospheric. Temperature increases towards depth. On the surface, bioaccumulation of elements in plants.

2. Bottom layer of the dump. Anaerobic conditions. Shale pyrite not yet oxidized. Some of metals and acidity from upper layer enters this layer. In case of availability of reactive limestone, acidity is neutralized. Precipitation can also occur due to anaerobic conditions only. Temperature controlled by oxygen diffusion, normally being 30–50°C in this layer. Leachate leaving this layer in short term is rich in SO_4^{2-}, Ca^{2+} and Mg^{2+}.

3. Self-ignition regions near the edges of the dump. Three stages may be separated in development of particular hot spot: incubation period with temperature rise until 70–80°C (only pyrite oxidizes), burning (active oxidation of organic matter) and cooling down. When cooled down (in order of tens of years after disposal), active leaching of metals starts from these regions, depending again from availability of limestone. Near the hot spot, thermal destruction of shale organic matter in anaerobic conditions may occur, producing liquid and gaseous organic substances-contaminants. In limestone-containing layers below cooled-down hot spot, Zn, Co and Ni are accumulating. Leaching from these regions contributes significantly to total pollution load in short term, as sulphates are formed in high rate.

4. Slopes of the dump. New-formed minerals (jarosite, gypsum, mixed-layer illite-smectite) occur in large extent. Clayey sediments are rich in Fe^{3+} (6–14%), precipitating in the form of amorphous hydroxide, and partly in jarosite, slope serving as redox front for outcoming waters. Concentration of metals (V, Mo, Cu, Ni, Zn) in these sediments on the slope of 10 years age however appear to be less than in original shale.

5. Ditches near the dump. Mine transport roads are in many cases presently serving as ditches filled or seasonally filled with water. In the bottom of these ditches, mud or peat is formed. Zn and P accumulate.

Conclusive remarks

Geochemical zonation of Maardu dump was carried out using theoretical approach and very few field analyses to describe an area of 10 sq km. These data should serve as preliminary ones for more detailed investigations. Key-question stands, how to account for buffering capacity of limestone with variable particle size in heterogeneous dump, assuming 3–6 times excess of limestone on overall scale in order to neutralize all acidity produced. Problems are not depleted in long term when all pyrite is oxidized and supposedly all acidity neutralized because of relatively low pH of natural precipitation (rainwater and snow melting water).

Regarding to pollution problems, V, Mo and U were considered as possible contaminants from the shale because of their initially high concentration in comparison with average in Earth crust. Analyses show, that these elements are not accumulating in larger concentrations as those in original shale after 10 years of changes in the dump. From environmental point however even several times lower than in the shale concentrations may possibly produce environmental hazards. This question needs to be separately discussed.

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MAARDU PUISTANGUTE GEOKEEMILINE TSONEERIMINE

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Resümee

Aastakümneid kestnud fosforiidi pealmaakaevandamine Maardus on viinud keskkonna reostumiseni, mille põhjustajaks on fosforiidikihi katendis sisalduv ja endisele karjäärialale tagasi kuhjatud *Dictyonema* argilliit. Argilliidis sisalduv püriit on atmosfääritingimustes ebastabiilne, reageerides hapniku ja veega. Oksüdeerumise tagajärjel tekivad sulfaadid, argilliit laguneb ja raskmetallid, mille sisaldus argilliidis on anomaalselt kõrge (U, Mo, V), vabanevad. Oksüdeerumisel eralduv soojushulk puistangute kuumenemiseni. Puistangute keskosas, kus hapniku juurdekannet kontrollib hapniku difusioon, jääb temperatuuritõus 20–30°C piiresse; puistangute äärealadel ja suurte lõhede või ebatasasuste olemasolul puistangu pinnal võivad tekkida konvektiivsed õhuvoolud. Need kiirendavad oksüdeerimisreaktsiooni, tagajärjeks on isesüttimine, kuna temperatuuridel 70–80°C algab argilliidis sisalduva orgaanilise aine (kerogeeni) aktiivne oksüdeerumine.

Puistangu üldises arengus võib eristada lühema- (aastad ja kümned aastad) ja pikemaajalisi (sajad ja tuhanded aastad) protsesse. Aastate ja kümnete aastate jooksul akumuleeruvad isesüttimiskollete alla jäävates kihtides (Zn, Fe, Co, Ni, orgaanilised ained), puistangute nõlvadel (Fe), ümbritsevates kraavides (Zn, P), isesüttimiskollete kohal (väljasettimisel gaasidest) ja puistangutaimedes (bioakumulatsioon) reoained. Toimub sulfaatiooni aktiivne väljakanne puistangualalt. Puistangute keskosas kulgeb redoksfront (keskmiselt 5 cm aastas) puistangute põhja suunas. Seoses puistangutesse kuhjatud lubjakivi neutraliseeriva toime tõttu püriidi oksüdeerumisel tekkinud väävelhappesse ja anaeroobsetele tingimuste tõttu puistangu sügavuses ei toimu esimeste aastakümnete jooksul raskmetallide aktiivset väljakannet. Puistangute heterogeensust arvestades on raske ennustada, kas lubjakivide puhverdusvõimest piisab kogu tekkinud happe neutraliseerimiseks. Arvestades aga, et 100–300 aasta pärast on redoksfront jõudnud puistangu alumistesse kihtidesse ning vihma- ja lumesulamisvesi on pidevalt happelise reaktsioo-

niga, võivad puistangud aastasadade möödudes olla ümbritsevale keskkonnale suuremaks ohuks kui praegu. Seetõttu ei ole korrektne leida mingi elemendi väljaleostumisaeg, viidates praegusele väljakande intensiivsusele.

Praegu võib puistanguala jagada viieks geokeemiliseks tsooniks: (1) ülemised kihid, kus argilliidi püriit on juba oksüdeerunud; (2) alumised kihid puistangu keskosas, kus valitsevad anaeroobsed tingimused; (3) isesüttimiskollete piirkond; (4) nõlvaalad; (5) ümbritsevad kraavid. Selle teoreetilis-praktilise tsoneerimise alusel on võimalik teha detailsemaid uuringuid selgitamaks reoainete akumuleerumist ja leostumist ning koostamaks pikemaajalisi prognoose.