

Groundwater Transport of Sulphates in the Estonian Oil Shale Mining Area

Merle Otsmaa, Tallinn University of Technology

Abstract – The development of Estonian power engineering on the basis of oil shale has caused several changes in the environment. One phenomena which accompanies oil shale mining is heightened content of sulphates in groundwater and surface water.

The aim of this research is to give an overview of groundwater and surface water transport of sulphates in the Estonian oil shale mining area and find out the regularity of its distribution during the time. As is known the aquifer containing the exploitable oil shale seam is influenced by mining activities the most, but also the quality of upper and lower aquifers can change. It is very important to clear up the vertical distribution of sulphates in different water-bearing horizons.

The phosphorite mining area which finished its activity in 1991 is also included in the research. The aim is to clear up to what extent environmental conditions have become better and draw conclusions on the ground of old closed mines for working mines for getting to know how much time it will take for self-cleaning of the environment.

Keywords – groundwater, mining, oil shale, sulphates.

I. INTRODUCTION

Oil shale production in Estonia started in 1916 [1]. At present, sixteen mines and open casts have been closed and two mines (Estonia and Ojamaa) are in production (Fig. 2). In addition to that, Narva and Sirgala opencasts are working. Oil shale mining causes several environmental problems. One of them is changing the composition of groundwater and surface water. Sulphate-ion is the most important indicator in the underground mining area [19]. The permissible content of sulphates by drinking water standard is 250 mg/l, or 350 mg/l in lower quality drink water. On ground of water analysis it is known that the baseline content of sulphates is 20 – 30 mg/l in natural groundwater.

II. HYDROGEOLOGICAL CONDITIONS

The hydrogeological properties divide the water-bearing formations into aquifers and aquitards (Fig.1). The layers of sedimentary rocks are sloping from the north southwards. The hydrogeological cross-section of the Estonian oil shale area consists of:

1. Quaternary aquifer system
2. Ordovician aquifer system:
 - a) Nabala-Rakvere aquifer;
 - b) Oandu aquitard;
 - c) Keila-Kukruse aquifer;
 - d) Uhaku aquitard;
 - e) Lasnamäe-Kunda aquifer;
 - f) Volhovi aquitard;

3. Ordovician-Cambrian aquifer system
4. Voronka and Gdov aquifer

Natural water is in all aquifers of $\text{HCO}_3\text{-Ca-Mg}$ or Mg-Ca type with a mineralization of 0.2 – 0.6 g/l. Only in deeper Voronka and Gdov aquifer is the water mostly of $\text{Cl-HCO}_3\text{-Na}$ type. The mineralization of that aquifer increases from west to east and is in the eastern part up to 1.3 g/l [1].

III. MINE IMPACT ON THE GROUNDWATER CHEMISTRY

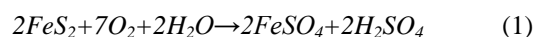
The productive bed of oil shale is a part of Keila-Kukruse aquifer. Due to mining technology, the table of groundwater has lowered below the level of oil shale stratum as a result of which a large depression cone is formed. In the areas where Keila-Kukruse aquifer is the first one from ground surface, the influence of dewatering extends to the distance of 1.5 – 2 km from the drainable area. Under the Nabala-Rakvere aquifer, the radius of depression cone of Keila-Kukruse aquifer is 5 – 6 km, at the same time in Nabala-Rakvere aquifer it is only 0.5 – 1.5 km. The lowering of Lasnamäe-Kunda aquifer extends to Lake Peipus in the south and to Narva River in the east.

Influx of oxygen transported into water-saturated layers raises the mineralization of ground water 2 – 3 times due to increasing of contents of sulphates, calcium and magnesium (Table I) [3]. Increased hardness is in the range of 10 – 16 mg.Eq/dm³.

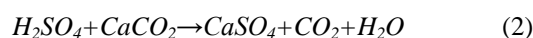
Significant enrichment of water with the sulphates takes place due to oxidation of pyrite. Sulphidic mineralization is associated with tectonic fissures what are running mostly in a northeastern-southwestern direction [1].

Only microcrystalline pyrite dispersed in the rock is suitable for oxidation [2]. Ordovician carbonate rocks consist 0.1 – 0.2% microcrystalline pyrite, oil shale 1 – 2% [4]. In mine water $\text{HCO}_3\text{-ion}$ is to a great deal replaced with $\text{SO}_4\text{-ion}$ (Table II). Reputedly the productive bed of oil shale consists of varying seams of kukersite and limestone. The formation of sulphates takes place in two stages.

I stage:



II stage:



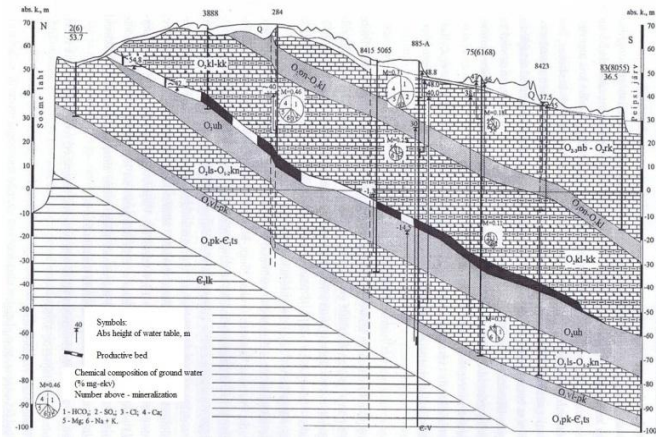


Fig. 1. Hydrogeological cross-section of the Estonian oil shale area [1].

TABLE I
TYPES OF GROUND WATER [5]

Type of water	Mineralization, g/l	SO ₄ content, mg/l	Origin of water
HCO ₃	0.3 – 0.4	< 20	Natural.
SO ₄ -HCO ₃	0.4 – 0.6	100 - 200	Inflow of Ahtme and Estonia mine, circle of influence of Sirgala opencast, outflow from Estonia mine and Viivikonna open cast.
HCO ₃ -SO ₄	0.8 – 1.0	200 - 600	Outflow from Ahtme and Sirgala, closed mines and dumps of Kohtla opencast.
SO ₄	2.5 - 8	1000-3000	Maardu phosphorite opencast.

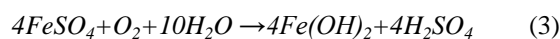
TABLE II
CHANGING OF WATER COMPOSITION

Indicator, %-ekv	Natural Ordovician water	Operating Estonia mine		Closed mine	Aidu opencast	Sphere of influence of opencast	Kohtla dump	Maardu phosphorite opencast	
		Overburden	Pumping station					Closed opencast	Burning dump
Mineralization	0,32	0,63	0,68	1,0	0,81	0,49	1,2	2,7	7,8
Na ⁺	3,0	1,0	2,0	2,0	2,0	3,0	2,0	0,5	0,5
K ⁺	1,5	0,5	1,0	0,5	0,5	1,0	0,5	0,5	1,0
Ca ²⁺	26	29	29	34	39	36	30	22	11
Mg ²⁺	20	19	17	13	11	9	19	27	38
HCO ₃ ⁻	45	30	26	20	19	27	14	6	2
SO ₄ ²⁻	1,5	20	22	26	28	11	33	44	48
Cl ⁻	2,0	1,5	2,0	3,5	2,5	5	2,5	0,5	0,5

The neutralization of acid takes place under the influence of carbonate rocks. Estonian oil shale – kukersite does not generate acid water. Its main impact on water bodies is an elevated concentration of sulphates [9].

Most of the mine shaft water samples with sulphate concentrations greater than about 1000 mg/l are close to saturation with gypsum [10]. During an experiment carried through in a South African mine, water containing 4 g/l H₂SO₄ and 582 mg/l Fe(III) was neutralized in the cone-shaped fluidized-bed reactor. Sulphate was removed from 4200 to 2000 mg/l as a result of gypsum crystallization. The level to which sulphate is removed is influenced by temperature, ion strength and the solubility of metal-calcium-sulphate complexes [11].

As Fe(II)SO₄ does not remain stable there will take place II stage of reaction:



The mineralization and composition of metamorphic water containing SO₄-ions is regulated by geochemical barrier which is for calcium sulphate 2.5 g/l. For easily dissolvable magnesium sulphate this barrier does not exist, but the

limitation factor is the low level of reactive pyrite. Therefore the mineralization of metamorphic water is about 1 g/l.

The ash emerging in power stations due to oil shale combustion contains over 10% free lime and is lead to dumps by hydro transport. Repeatedly used water reaches the mineralization up to 5 g/l. The SO₄ content of water is up to 3500 mg/l, Ca-content up to 2000 mg/l and pH 12.5 [5], by other data the SO₄ content of waste water in sedimentation basins of Baltic power station is up to 4200 mg/l, mineralization 15 – 19 g/l. In the area of ash fields of power stations and chemical concerns the sulphate pollution is observed also in Ordovician-Cambrian aquifer system.

In the mining area it is possible to distinguish natural, natural-technogenic and technogenic aeration zones. The natural aeration is located higher than the natural ground water level in untouched rock layer. The preliminary pyrite has a long time ago oxidized, and formed sulphate-ions are carried away with infiltration water [7]. A natural-technogenic aeration zone is formed in the area of depression cone in rock layer untouched by mining operations. In dewatered layers pyrite will fall under the influence of oxygen and the increased amount of SO₄-ion is observable already in case of small content of pyrite, for example in wells 1 – 3 km from Aidu opencast. The technogenic aeration zone will form in broken

rock massive where the oxidation is taking place more intensively and the formed SO_4 -ions will be easily carried away by water. The $\text{HCO}_3\text{-SO}_4$ Mg-Ca water is formed (Tables I, II).

Technogenic groundwater is formed in dumps of opencasts and in depleted mining area. Dewatering of the aquifer increases the thickness of aeration zone and an oxidizing environment will be formed.

IV. THE TRANSPORT OF SULPHATES

The water of mines and opencasts is pumped out into sedimentation basins where suspended matter will be deposited. From $\text{Fe}(\text{OH})_3$, the oxidation product of pyrite, will form Fe_2O_3 what will be deposited therein. It is testified by red colored limestone pieces in Viivikonna opencast. But SO_4 -ion is carried away with groundwater and surface water drain. Henceforth the sulphur will be bound with calcium and magnesium, no more with iron like in pyrite. Sulphate is highly soluble under all temperature and pH conditions, whereas sulfide solubility is pH-dependant [12]. Sulphate concentrations will be lowered mainly through mineral precipitation (gypsum) or biological assimilation into plant or microbial tissue. Rates of sulphate reduction depend on pH, redox potential, type and quantity of available organic matter and the ratio of organic carbon to sulphur. Higher organic carbon concentrations increase sulphate reduction.

From sedimentation basins the mine water is directed into Purtse and Vasavere Rivers and by Roostoja River into Rannapungerja River (Fig. 2). From Narva and Sirgala opencasts the water flows into Mustajõgi River and further into Narva River. Jõhvi ditch, Kose and Sanniku streams are draining Tammiku and Ahtme closed mines and are flowing into Rausvere River which leads its water into river Pühajõgi. A part of mine water is led by ditches springing from the west and the east into lakes Konsu and Kurtna [1]. In the region of oil shale mining on an average 15 million m^3 of water is being pumped out of mines monthly [14].

A. Water in Closed Mines.

Water outflow from Käva mine takes place by its southwesterly ditch into Kohtla River (Table III). The area of closed Kiviõli mine is situated on the territory of Kiviõli oil shale plant, which has been an essential and long-time source of pollution. The northern part of the mine is isolated by railway from the southern part. Mine water of the northern part passes through the plant's pumping station and water-purification of Kiviõli town. South side water flows out by gravity, pervades Küttejõu opencast and falls into Purtse River.

Separated from each other, the closed mines are partially filled with water. Water changing through the safety pillars between mines is not excluded. The mineralization of water of the Kukruse mine was 1.3 g/l and sulphate content 500 mg/l, but during ten years (1985 – 1995) the mineralization decreased up to 0.77 mg/l and sulphate content till 176 mg/l. Dynamic of water quality in closed mines is not investigated enough and it demands further researches [1].

Observations of critical changes in water quality of the closed mines are made by Geological Survey of Estonia. The

mineralization of water increased and exceeded even 2 g/l, hardness 15 – 20 mg.Eq/l and sulphate content 500 mg/l. It has also been estimated that if the groundwater table rises higher than 45 – 47 m, the water in Ahtme mine field will affect the water level and quality in the Vasavere intake. According to prognoses, after filling the mine with water over 8 – 10 years, the groundwater flow will be directed towards buried valley. This creates conditions for deterioration of water quality in Vasavere intake because of organic compounds inflow from bog water and maybe also due to the mine water. The content of sulphates, ammonium and calcium can increase in the water intake.

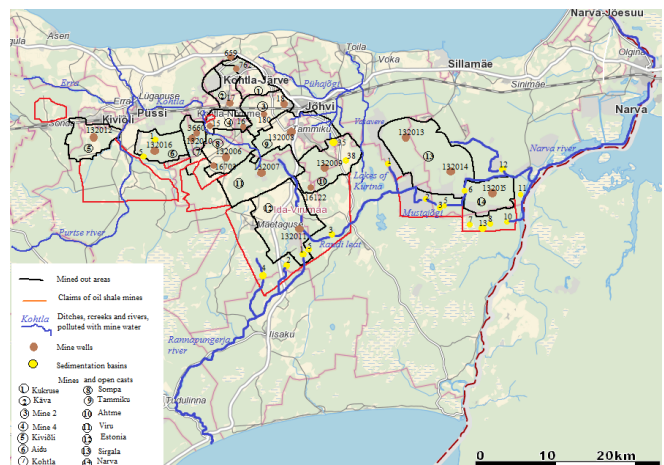


Fig. 2. The boundaries of oil shale mines and water bodies influenced by mining activities.

V. THE STATE OF RIVERS AND LAKES

From 1992, the water quality of rivers is regularly monitored. Water composition is analyzed primarily once a month. In observable Alajõe River there is in average 21 mg/l sulphates and in Tagajõgi 19 mg/l. In the mouth of Narva River there is 21 mg/l sulphates and in the head 17 mg/l (Fig. 2) [18]. Some rise of sulphates is noticeable in Kunda and Selja rivers; the contents are accordingly 43 and 56 mg/l. An extremely high content of sulphate was measured in Kunda River in June of 2009 – 230 mg/l. During the years the average content of sulphates in rivers Roostoja and Pühajõgi is 181 mg/l. In Pühajõgi especially high sulphate content was ascertained from summer 2005 till late autumn 2008: the average content was 302 mg/l and the highest in August-September 2006: 470-480 mg/l.

The most abounding in sulphates are waters of the rivers Mustajõgi and Purtse: the average contents 289 and 282 mg/l, respectively. The water composition of Purtse River is influenced by former Kiviõli mine and Aidu opencast. Mustajõgi flows through the Narva opencast. The water of Mustajõgi is analysed since 2001. Higher contents cleared out during the years 2006 – 2008 (the highest in August of 2007 - 580 mg/l). There is no data for 2009. In 2010 and 2011 the samples were taken more seldom than earlier.

In Purtse River higher average contents were found in years 2002 and 2003, when there were sulphates at the levels of 466 and 373 mg/l, respectively. The highest contents in samples

were over 600 mg/l. Since 2008, the amount of sulphates in Purtse River has decreased (274 – 220 mg/l).

In the area where the mines and opencasts are situated is the buried valley of Vasavere with 42 lakes of Kurtna (Fig. 3). Here is also Vasavere water intake with its numerable bored wells which get their water from a Quaternary water system. The high-quality subsoil water is connected with a lot of lakes and also with Ordovician groundwater which is drained by Ahtme and Estonia mines in the west and Sirgala opencast in the east. In order to avoid lowering of the water table of subsoil and lakes there is grounded on the range of 5.1 km 5 – 15 m wide and 2 – 5 m deep infiltration basins for water pumped out from opencast.

Mine water is flowing from Estonia mine by Raudi watercourse into Lake Nõmmejärv, passing lakes Särgjärv and Ahvenjärv. Lake Suurjärv gets its water from Vasavere river where is directed Ahtme mine water. Since 1980 a persistent rise of sulphate content (up to 190 mg/l) is observed in Lake Konsu. Sulphate content in Nõmmejärv was 355 mg/l in 2006. Compared with the year 1953, there were only 16 – 21 mg/l of sulphates. Water samples are also taken from lakes Martiska, Kuradijärv and Kurtna Valgjärv, but there was sulphate content within the range of 10 – 20 mg/l.

Active transformation of the water body takes place in lakes with restricted water change. In 1937, the mineralization in Nõmmejärv was 0.2 g/l and SO₄ content 5 mg/l, after inflowing of mine water accordingly 0.65 g/l and 300 mg/l [7]. In the Finnish Gulf there have always been acidic conditions but in lakes develop local reducing zones. In the case of heightened SO₄ content, H₂S begins to form. If there is not enough iron for binding of H₂S in the water or lake mud, it will spread in the entire reducing zone influencing perniciously on ecosystem of lake.

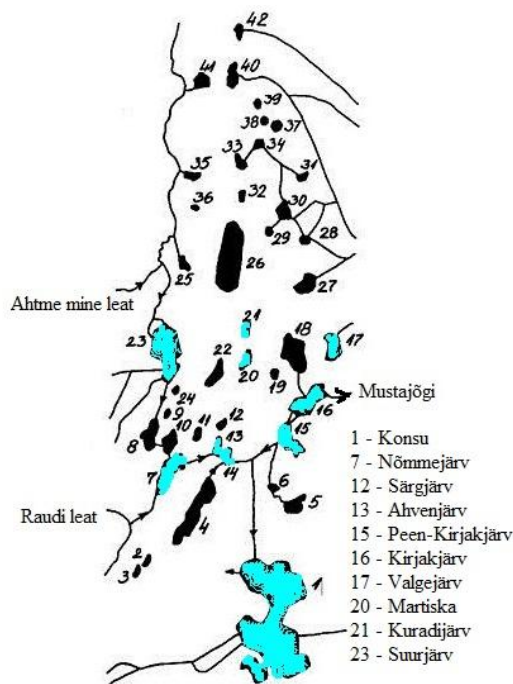


Fig. 3. Observable lakes of Kurtna

Accruing municipal water abounding in organic matter will intensify this process and form a „dead, zone. These zones are not formed in Lake Peipus thanks to the large amount of water, but water quality is nevertheless becoming worse.

VI. SULPHATES IN GROUNDWATER

The transport of sulphates takes place not only by streams and rivers but also by groundwater. The piezometrical level of Keila-Kukruse aquifer lowers southwards and eastwards, consequently the groundwater is also flowing in that direction. Any essential increase of sulphates in wells away from the mining area is not noticed. Evidently most of the SO₄-ions are moving with the surface water.

The overview of the state of the groundwater is based on the analyses of 140 wells of the period of the years 1959 – 2010 [17]. Water samples are taken very irregularly, from some wells only one sample during the entire period. Water samples are taken from different aquifers therefore is possible to make conclusions about their quality separately. Most of the samples are taken in the years 1980 – 2000 when oil shale was excavated in the largest capacity. Later observations of water quality have been hindered by several political and economic issues. Unfortunately the termination of taking water samples does not mean that water quality has normalized or that no observation is necessary.

The largest content of sulphates is principally in mine water in the time period 1970 – 2000. Henceforth water samples are taken only from Viru and Kiviõli mines and Aidu opencast. The highest sulphate contents were observed in 1975 in Sompä and in 1989 in Kiviõli mines, at the levels of 1184 and 1241 mg/l, respectively. In 1988 in Viivikonna opencast the sulphates were observed at a level of 1083 mg/l.

On the basis of existing water analyses the tendency of increasing sulphate contents is noticeable, but in time period of 1990 – 2000 has also been observed sulphate concentrations decline at places. Out of the mining area, the water quality meets the requirements of the drinking water standard. For example, in the boundaries of Vasavere buried valley, the sulphate content is mostly less than 10 mg/l or at least less than 100 mg/l.

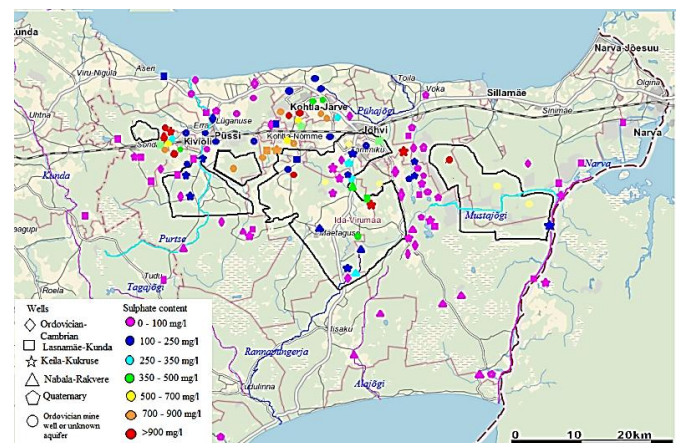


Fig. 4. The highest sulphate contents through the ages in groundwater and rivers.

The highest sulphate contents through the ages are presented in Figure 4. The most polluted areas are opencasts and old mines, nearness of sedimentation basins and pumping stations.

In Vasavere water intake, the most sulphate-rich water was ascertained in 1980 and in 1997 containing 137 mg/l and 165 mg/l sulphates.

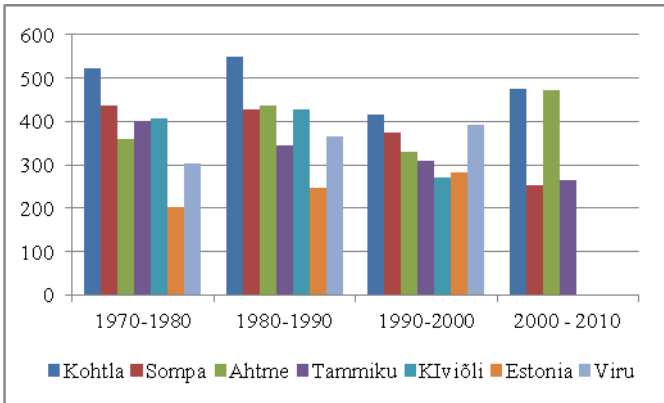


Fig. 5. Sulphate contents of Keila-Kukuruse aquifer in mines, mg/l.

In mine water the SO₄ content has been 24.3 – 1642 mg/l; in wells 31.7 – 846.7 mg/l. The maximum contents are ascertained in waste water purification installations [6].

A. Sulphate distribution in different aquifers.

Ordovician-Cambrian aquifer is more protected from impact of human activity than the upper aquifers. The most affected in mining area is the Keila-Kukuruse aquifer owing to exploitable oil shale. Based on data of neighboring wells opening different aquifers in most cases the Keila-Kukuruse aquifer is richer in sulphates than the Lasnamäe-Kunda aquifer. In many cases the contents are more or less equal. In Figures 5 and 6 we can see that in Kohtla mine the Lasnamäe-Kunda aquifer is even more contaminated than the Keila-Kukuruse aquifer. In Tammiku and Ahtme mines the situation is reversed. Also Ordovician-Cambrian aquifer includes usually less sulphates than Keila-Kukuruse aquifer. Compared with Nabala-Rakvere aquifer Keila-Kukuruse aquifer includes sulphates to a lesser extent. Evidently it is caused by good availability of oxygen in the aeration zone of the upper rock layers. High pollution in some cases can also reach the deep aquifers, for example an Ordovician-Cambrian well in Varinurme village of Sonda forest district (SO₄ content 910 mg/l) (Fig.6). In the same village the Lasnamäe-Kunda aquifer (459 mg/l) and a Keila-Kukuruse well (950 mg/l) are strongly polluted. In the old pumping station of the Kohtla mine both the Lasnamäe-Kunda and Keila-Kukuruse aquifers (466 and 476 mg/l) are equally polluted. However, in Edise village the sulphate content of Ordovician-Cambrian aquifer is essentially lower (85 mg/l) than in the Keila-Kukuruse well (290 mg/l) of the same village.

B. Time dependent sulphate distribution.

Evidently the observation of water quality changes in the mining area is only observed since the 1960. At that time, heightened sulphate content is noticeable in the region of Tammiku, Viru and Sompa mines. In the seventies the

sulphate content also increased in the northern part of Vasavere valley, since water pumped out from the Ahtme mine was lead into Vasavere River. In the 1980s further enriching of water with sulphates takes place and in the 1990s the pollution expanded in the area of Estonia mine. In Atsalama village the average sulphate content was 289 mg/l, the maximum in spring 1996 in Nabala-Rakvere aquifer was 473 mg/l.

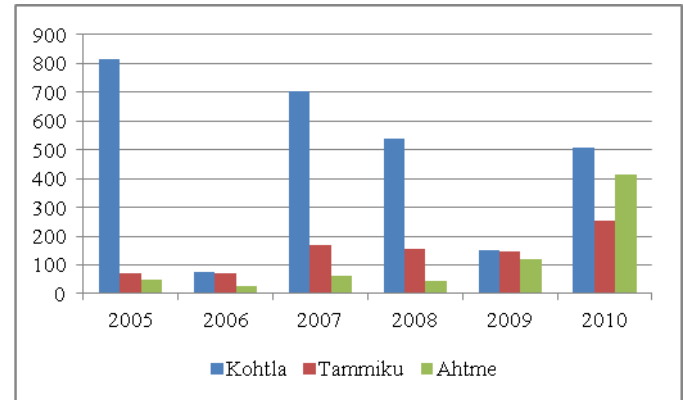


Fig. 6. Sulphate contents of Lasnamäe-Kunda aquifer in mines, mg/l.

Long-term observations have shown that water quality in closed mines (Kiviõli, Sompa, Tammiku) has begun to improve (Fig. 5). However in operating mines, the sulphate contents are rising (Estonia, Viru). On the whole, water composition is slowly improving.

It is argued that purification of water is best described by the exponential function [14]. The time period during which the content of sulphates decrease twice, is about 1.8 years for sulphates and in about 5 years after the closure of a mine the content of sulphates ought to be decreased below the maximum permitted level in drinking water (250 mg/l).

TABLE III
WORKING YEARS OF OIL SHALE MINES

Mine	Work started	Closed
Kukuruse	1916	1967
Kiviõli	1922	1988
Käva	1924	1973
Kohtla	1937	2001
Ahtme	1948	2002
Sompa	1949	1999
Mine 2	1949	1974
Tammiku	1951	1999
Mine 4	1953	1975
Sirgala	1963	
Viru	1965	2012
Narva	1970	
Estonia	1972	
Aidu	1974	2012

Unfortunately we cannot see it on the grounds of available data. In Tammiku mine the sulphate content has decreased during 10 years only about 50 mg/l, which is a sixth of the whole amount. In order to decrease as much, it will probably

take 30 years. In Sompma mine the decrease of sulphate during the same period has been about 100 mg/l.

Analyzing the changes of sulphate content in river water is clearly to see the regularity according to which the minimum sulphate contents appears in April, maximum contents in August and September. Higher contents are characteristic also in June, July and October. Evidently the reason lies in precipitation intensity.

Surveys have been irregular. Mainly water samples are not taken in January, February, November and December.

VII. MAARDU PHOSPHORITE MINING AREA

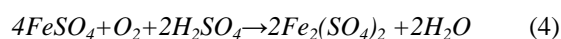
Phosphorite was excavated in the neighborhood of Maardu, in Ülgase occurrence by underground mining method in the period from the years 1926 – 1938. The Maardu phosphorite mine was operating from 1940 – 1965. In 1954 excavating started in the Northern opencast and in 1975 in the Southern opencast. At the end of 1990 the area of excavated opencast was 13 km². In May 1965 underground mining of the ore was finished and all the phosphorite producing ended in 1991. The purposeful environmental investigations began in 1993 in Maardu.

The main source of reactive pyrite is in Maardu Dictyonema argillite which contains 4% pyrite. Argillite makes 1/3 of the mass of dumps. Dump water is SO₄ Ca-Mg type with mineralization >2.5 g/l [7]. The total area of Maardu dumps is 10.6 km², every square meter containing on the average 7 tons of shale opened to the access of atmospheric oxygen [16]. Unlike the conditions in the oil shale area, there is nothing in this location for neutralization of H₂SO₄.

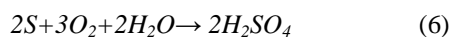


Fig. 7. Location of Maardu phosphorite opencast

Oxidation of FeSO₄ in acidic milieu takes place only by means of bacterium *Thiobacillus ferrooxidans* [5].



Iron (III) sulphate is in acidic milieu a potent oxidizer of pyrite. Free sulphur oxidizes by the agency of air oxygen by means of *Thiobacillus ferrooxidans*



In Maardu opencast the oxidation of pyrite took place more intensively because the carry off of oxidation products was quick and more complete than in case of pyrite oxidation in carbonate rocks where Fe(OH)₃ precipitates on the spot (red-colored limestone pieces in Viivikonna opencast).

During the mining period in Maardu three pumping stations were in operation and the water was directed directly into Muuga bay or Lake Maardu. Regional groundwater flow is from the south to the north, the direction of opencast water from the east to the west (to the underground mine and Kroodi stream). The local watershed is in the area of Ülgase village where a part of the water flows towards opencast and another part in the direction of clint. Lake Maardu has been the main reservoir of technological water for the chemical plant of Maardu [7]. The inflow to Lake Maardu consisted in the ground of data from 1977:

- 1) Natural inflow (precipitations, ground- and surface water) – 4.55 mln m³;
- 2) Artificial flow (Jöelähtme River) – 2.4 mln m³;
- 3) Opencast water – 7.31 mln m³.

There are two aquifers in Maardu district:

- 1) Ordovician limestone and sandstone, base Dictyonema argillite;
- 2) Ordovician-Cambrian sandstone, base Cambrian blue clay [8].

On the area of opencast the upper water system is absent and the lower aquifer is free surfaced, its upper part is formed in dumps. Opencast represent a big depression cone dewatering Ordovician aquifer. The watershed is situated more or less in the center of the investigated area. In the opencast there has formed a stabile hydrogeological regime; the inflow is equal to outflow.

TABLE IV
WATER COMPOSITION IN MAARDU [7]

Origin of water	pH	Mineralization, g/l	SO ₄ , mg/l
Water of burning dump	1.8 – 2.5	15 - 70	3500-55000
Water of burned dump	2.7 – 7.5	0.1 – 3.0	10 - 2200
Water of not-burning dump	2.8 – 3.0	3.4	2300 - 3000
Groundwater in burning zone	6.7 – 7.2	6 - 8	4000 - 6000
Groundwater out of burning zone	7.0 – 7.5	0.3 – 0.6	20 - 200
Opencast water	7.0 – 7.6	0.7 – 3.5	350 - 2300
Lake Maardu	7.8 – 8.6	0.45 – 0.65	200 - 300
Kroodi stream	6.7 – 8.1	0.9 – 1.8	440 - 650

TABLE V
IMPROVED WATER QUALITY

Place	Time	pH	Mineralization, g/l	Sulphates, mg/l
Boreholes	1984 - 90	7.46	3.2	2210
	1996	7.1	3.5	2092

Trench	1984 - 90	8	8.9	5921
	1996	8	4.3	2775
Outflow from old mine	1994	6.6	4.6	2921
	1996	6.8	3.9	2740

Water level is changing on a scale of 0.1 – 0.5 m. The absolute height of the water table in trenches and dumps was 31 – 33 m, in a depth of 10 – 17 m from the ground surface. The water of trenches and boreholes do not essentially differ in their chemical composition. Vertical filtration from dumps to sandstone is small.

In course of investigations of 1996, the quality of opencast water was determined, as was the quality of surrounding ground- and surface water. The investigations were carried through by AS Geotehnika Inseneribüroo. 15 bore holes were made, water samples were taken two times from ten observation points. The results of the analyses of opencast water were compared with analyses from the 1980s where it was possible to notice some improvement of the state of opencast water. The sulphate content was about 5600 mg/l in the period of 1984 – 1990 and in 1996 it decreased to 3100 mg/l. (Table IV [8]).

In 2010, a water sample was taken in observation point 12 (Fig. 8). Analyzing this sample with field laboratory sulphate content about 1200 mg/l was ascertained. In 1977 this substance was 1130 mg/l. In Kroodi stream the sulphate contents have been: in year 1977 – 584 mg/l, 1996 – 280 mg/l, 2012 – 627 mg/l [18].

The water in local dug wells is not much influenced by phosphorite mining but by other factors. The highest sulphate content was in a well of Vainu homestead in Rebala village (375.9 mg/l) which does not meet the drinking water standard (Fig. 8) [8].

On the basis of data from the Estonian Environment Information Centre, heightened sulphate content is observed in Maardu town, primarily near to Lake Maardu. Water analyses are made in the years 1998 – 2006 and the sulphate contents in Silurian-Ordovician and Ordovician-Cambrian aquifers are mainly over 100 mg/l, the highest 229 mg/l in July 2003. In Vandjala the Silurian-Ordovician water contains sulphates 40 – 75 mg/l, Ordovician-Cambrian water in Rebala and Manniva villages up to 56 mg/l which is not common for completely unspoiled water composition. Cambrian-Vendian water contains sulphates mainly less than 10 mg/l, nowhere over 20 mg/l. Unfortunately, only one analysis is made for each well, and therefore it is not possible to observe changes in water composition.

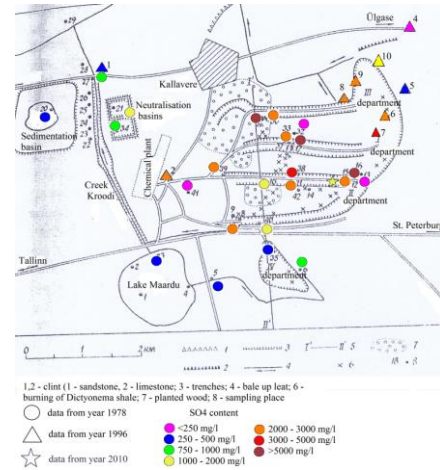


Fig. 8. Researches in Maardu phosphorite opencast.

On the basis of some data [20] the mineralization of mine water was 0.65 g/l in 1945 and 3.0 g/l in 2001. Through the burning argillite washed water had mineralization up to 67 g/l (1977), among them sulphate content up to 50 g/l.

VIII. WATER SULPHATE CONTENT REGULATION METHODS

Biological treatment with sulphate-reducing bacteria (SRB) has been considered as the most promising alternative for acid mine drainage (AMD) decontamination [13]. SRB have the ability to reduce sulphate to sulphide and this sulphide reacts for example with copper, iron and zinc, forming insoluble precipitates. Heavy metals are generally toxic for microorganisms. Toxic concentrations for SRB range from a few ppm to as much as 100 ppm. The experiments verified that sulphate was completely reduced after 20 days in water with iron content smaller than 0.4 g/l. It has been reported that the characteristic toxic concentration of zinc for SRB is 13 – 40 mg/l. But no growth of SRB observed at 2 mg/l of copper.

Another possibility is to remove sulphates from mine water by precipitating BaSO₄ with BaS [15]. Untreated mine water with SO₄-ion of 2060 mg/l contained after neutralization with lime 1970 mg/l SO₄. BaS addition decreased SO₄ ions content to 120 mg/l.

Gas Redox and Displacement System (GaRDS) is an approach devised for stabilizing sulphide minerals by manipulating the atmosphere in mining voids. Not only can these gas mixtures halt sulphide oxidation and acid generation, but they can result in the precipitation of secondary sulphides from the accumulated drainage water. GaRDS displaces air from the mining voids by introducing biogas to the mine once all shafts have been closed. The biogas is comprised of carbon dioxide and methane. The GaRDS technique physically displaces oxygen and chemically reverses the acid generation reactions and stabilizes the acid producing minerals.

IX. CONCLUSIONS

The tendency of pyrite oxidation is expanding as ever more new exploration fields are taking into use, but in extracted fields the oxidation process does not completely cease [1]. On the basis of observations pyrite oxidation is slow.

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 [16]. Low-temperature oxidation is undesirable because of acidity generation, water pollution and potential bioaccumulation effects and should be minimized by guaranteeing anaerobic conditions inside the shale disposal site.

Mine water loses in the sedimentation basins and ditches an essential part of suspended solids but carries in water bodies the entire sulphur in the form of SO_4 -ion. In oxidizing environment SO_4 -ion is stable and harmless but in reductive conditions as H_2S , very toxic and causes a major damage [5]. Owing to oxidation process of pyrite and as a result of dewatering when 230 – 260 mil m^3 water yearly with SO_4 -ion content of 200 – 500 mg/l is pumped out from mine every year 15 – 40 thousand tons technogenic sulphur get into geochemical circulation.

In order to develop the right conclusions, the amount of initial data is too small. Water samples are taken quite seldom and occasionally. On the grounds of these samples the prognoses about improving the state of the water are not very optimistic. Decreasing sulphate content does not occur very quickly. In some cases it may even rise in recently closed mines (Fig. 5). In Maardu the situation has considerably bettered (Table V), but not in Kroodi stream. As a rule, the samples in different times are not taken from one and the same place which makes it difficult to make accurate inferences.

It is necessary to keep an eye on the fact that in nature the balance between mobile and immobile forms of elements is regulated with geochemical barriers. However no barrier exists in nature for effective elimination from circulation of technically-created mobile elements. This balance is also possible to achieve in a technical way, establishing water purification facilities.

REFERENCES

1. **Kattai, V., Saadre, T., Savitski, L.** Eesti põlevkivi: geoloogia, ressursid, kaevandamistingimused. Eesti Geoloogiakeskus, Tallinn, 2000. 226 p.
2. **Driver, G.** Geochemie of natural water. Moscow: Mir, 1985. 439 p. (in Russian).
3. **Savitski, L.** Peculiarity of forming water inflows into mines of Estonian oil shale area. In: Problems of Estonian hydrogeology. Tallinn, 1980, p. 152-162. (in Russian).
4. **Baukov, E.** Substantial composition of oil shale basin. Tallinn, Institute of Geology, 1958. 163 p. (in Russian).
5. **Johannes, E., Karise, V., Pill, A., Erg, K.** The role of anthropogenic factor in forming of the groundwater composition in Northeastern Estonia. Tallinn, EGF 4206, 1985. 123 p. (in Russian)

6. **Karise, V., Laane, L.** Contamination and self-purifying in North Estonian industrial area. Tallinn, EGF 3228, 1970. 249 p. (in Russian).
7. **Karise, V., Johannes, E., Punning, J.-M., Pill, A.** The impact of phosphorite production residues on environment. Tallinn, EGF 3542, 1978. 111 p. (in Russian).
8. **Sedman, P.** Maardu Põhjakarjääri hüdroteoloogiline monitoring. Tallinn, AS Geotehnika Inseneribüroo aruanne, 1996.
9. **Puura, V., Puura, E.** Origins, compositions, and technological and environmental problems of utilization of oil shale. Tartu, University of Tartu, 2007.
10. **Gammons, C., Metesh, J., Snyder, D.** A survey of the geochemistry of flooded mine shaft water in Butte, Montana. In: Mine Water and the Environment, 2006, p. 100-107.
11. **Maree, J., Plessis, P.** Neutralization of acid mine water with calcium carbonate. Wat. Sci. Tech. Vol. 29, No. 9, 1994, pp. 285-296.
12. **Sturman, P., Stein, O., Vymazal, J., Kröpfelova, L.** Sulphur cycling in constructed wetlands. In: Wastewater Treatment, Plant Dynamics and Management in Constructed and natural Wetlands, 2008, pp. 329-344.
13. **Martins, M., Faleiro, M.L., Barros, R.J., Verissimo, A.R., Barreiros, M.A., Costa, M.C.** Characterization and activity studies of highly heavy metal resistant sulphate-reducing bacteria to be used in acid mine drainage decontamination. In: Journal of Hazardous Materials 166, 2009, pp. 706 – 713. <http://dx.doi.org/10.1016/j.jhazmat.2008.11.088>
14. **Erg, K., Reinsalu, E., Valgma, I.** Geotechnical processes and soil-water movement with transport of pollutants in the Estonian oil shale mining area. Rezekne. – *Proceedings of the 4th International Scientific and Practical Conference "Environment. Technology. Resources"*. 2003, pp. 79-84.
15. **Bosman, D., Clayton, J., Maree, J., Adlem, C.** Removal of sulphate from mine water with barium sulphide. Mine Water and the Environment 2006, pp. 149-193.
16. **Puura, E.** Oxidation of Dictyonema shale in Maardu mining waste dumps, 1998.
17. Elis veka website, Available: <http://loodus.keskkonnainfo.ee/WebEelis/veka.aspx?type=artikkel&id=214457803> [Accessed: 09.10.2013]
18. Keskkonnaseire korralduse osakond Available: <http://seire.keskkonnainfo.ee/> [Accessed: 09.10.2013]
19. **Erg, K.** Groundwater Sulphate Content Changes in Estonian Underground Oil Shale Mines. Thesis on Power Engineering. Tallinn, 2005, 39p.
20. **Erg, K.** Maardu North Career foreclosure – plan, design and reality. TTU, 2001, 33 p.



Merle Otsmaa has studied geology in Tartu University in years 1985 – 1990. She acquired the profession of geological engineer. After finishing of the university she started work at Geological Survey of Estonia. From the year 2010 Merle Otsmaa has been connected with Tallinn University of Technology.

The five-years-lasting studies have given her M.Sc. degree. In the year 2010 Merle Otsmaa began to work for her doctor's degree on specialty of geotechnology.

Merle Otsmaa has worked in Geological Survey of Estonia as a hydrogeologist and she has been engaged in research works of groundwater contamination. She has also composed digital maps of Estonian mineral resources. As doctoral student Merle Otsmaa has devoted herself to investigations of stability of mined areas and several hydrogeological problems connected with oil shale mining in Estonia.

Address: Ehitajate tee 5, Tallinn, EE-12618, Estonia

E-mail: merleotsmaa@gmail.com