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CHANGES IN PHYSICO-CHEMICAL COMPOSITION OF MINE WATER IN CLOSED *KIVIÕLI* OIL SHALE MINE

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The changes in physico-chemical composition of mine water flowing out from the now closed Kiviõli mine in 1988-1996 concerning sulfates, chlorides, calcium, magnesium, sodium, potassium and total hardness have been studied. Annual average values of these parameters are in a clear correlative function: the correlation coefficients lie within the range of 0.8367-0.9993. Considerable differences in the hydrogeological and geochemical processes running underground after closing the mine have caused up to threefold decrease in the content of above-named components in the mine water. As a result, the mine water flowing out is relatively pure at the present time and does not essentially damage the quality of water in Purtse River any longer. There is no oil and phenolic pollution in presently outflowing mine water, whereas during the closing of the mine the isolation of the part of mine (pit bottom) that remained under the territory of Kiviõli Oil Shale Processing Plant from all mined area, was accomplished effectively.

Introduction

Kiviõli oil shale mine that started its activity in 1922 was finally closed in 1988. During 65 years of mine operations, a large mining field with an area of about 25 km² was formed, with a maximum mining depth of 28 m and thickness of mined mineral layer up to 2.2 m. As a consequence of oil shale mining, the Ordovician aquifer system has been totally drained; in order to ensure the work of the mine, inflowing groundwater and precipitation water (60-70 % from total water quantity) were to be pumped out as mine water and directed into the rivers of Purtse Basin (Hirmuse and Purtse rivers) continuously. About 25-34 million m³ of mine water were pumped out yearly, depending on meteorological conditions and season.

A distinctive peculiarity of water pumped out from *Kiviõli* mine was a relatively high content of volatile phenols and oil products, amounting to 0.250 and 0.450 mg/L respectively [1]. It was caused by the circumstance that the pit bottom of previous *Kiviõli* mine was directly located under the territory of *Kiviõli* Oil Shale Processing Plant (*Kiviõli* OSP, by now subordinated to AS *Kiviter*). In the course of many years the shale oil on the ground around the plant installations was continuously soaked with rainwater underground (without any monitoring), and was distributed with mine water to many remote mining galleries. At the time of closing the mine, it became necessary to solve this problem in order to avoid future pollution of groundwater (mine water).

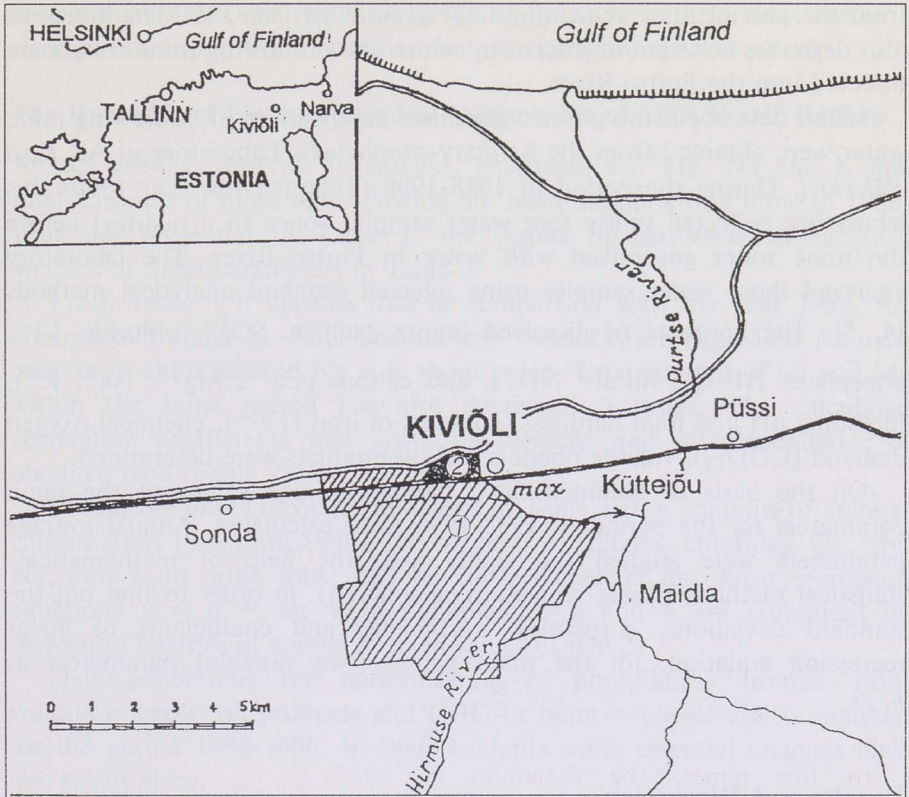
For this purpose, the pit bottom area was isolated from the remaining part of the main mining area to block the further distribution of organic pollution from under the plant. After finishing all works, the mining galleries were filled with water and mine waters from underground were directed into the *Purtse* River through a ditch system.

It is clear that after closure of the mine and its filling with water, the underground hydrogeological and hydrochemical situation of previous mining area would change completely. Simultaneously the hydrochemical and geochemical processes in water movement within closed mine had to change, causing numerous differences in chemical composition of mine water.

In this paper, the dynamics of changes in physico-chemical composition of mine water flowing into the *Purtse* River during the period of 1988-1996 after closing the mine is analysed briefly. It includes an assessment of situation in underground environment that inevitably causes transformations in water chemical composition but simultaneously can mitigate the negative effects of technogenic water cycling that were formed during the operation period of *Kiviõli* mine. It is the first time that such analysis was carried out.

Study Area

The presently closed *Kiviõli* mine is located in the western part of Estonian industrial oil shale deposit and its mining field covers the territories of *Sonda* and *Maidla* rural districts of *Ida-Viru* County (Figure, shaded area). Practically all mined area lies south to *Tallinn-Narva* railway but a minor part remains northwards of the railway, extending until the *Sonda-Kiviõli* local road. Small darker part in the northern part of shaded area indicates the pit bottom area under the territory of *Kiviõli* OSP, which is watertightly isolated from the remaining part of the mine. Underground water outflow into the *Purtse* River is marked with an arrow.



Sketch map of closed *Kiviõli* mine region: 1 - mined area, 2 - pit bottom area under the territory of *Kiviõli* OSP; - - - - maximum level of water flux in mine galleries (41.5 m abs.)

Outflow occurs by ditches with a total length of about 500 m which have been excavated on the territory of the previous *Küttejõu* oil shale open pit. The maximum level of water flux (rise) after mine's filling is shown with a dotted line on the shaded area. In this case, the water quantity in the mining galleries reaches up to 11 million m³.

Materials and Methods

A synopsis of technical solutions for closing the *Kiviõli* mine and generating the optimum hydrogeological regime in the mining galleries was drafted on the ground of design documentation compiled by the Projection-construction Bureau of AS *Eesti Põlevkivi* in 1987-1988 [2, 3]. According to the blueprint, two watertight concrete partitions in the mine level road were envisaged in order to prevent the distribution of pollutants (oil products, phenols) to the southern mining galleries with mine water,

from the part of mine remaining underground Kiviõli OSP. The blueprint also describes a system of ditches by which the outflowing mine waters are directed into the Purtse River.

Initial data about the physico-chemical composition of outflowing mine water were obtained from the Sanitary-prophylaxis Laboratory of AS *Eesti Põlevkivi*. During the period of 1988-1996 (excepted the year 1990) this laboratory collected yearly four water samples (once in a quarter) before the mine water got mixed with water in Purtse River. The laboratory analyzed those water samples using selected standard analytical methods [4, 5]. The contents of dissolved anions (sulfate SO_4^{2-} , chloride Cl^- , phosphate HPO_4^{2-} , nitrate NO_3^-), and cations (Ca^{2+} , Mg^{2+} , Na^+ , K^+), including pH and total hardness, contents of iron (Fe^{3+}), chemical oxygen demand (COD_{Cr}), volatile phenols and oil products were determined.

On the basis of obtained data, annual average values of the main parameters for the period of 1988-1996 were calculated. Annual average parameters were studied thoroughly with the help of mathematical-statistical methods (linear regression calculation), in order to find out the standard deviations, correlation coefficients and coefficients of linear regression equation, for the main paired (two variable) parameters as x, y).

Results and Discussion

The Groundwater Movement in Closed Mine

From the hydrogeological aspect, the basic solutions for closing the *Kiviõli* mine should be evaluated as successful. The most polluted section of mining area - pit bottom under the territory of Kiviõli OSP - is isolated by watertight concrete partitions from remained part of mined area. The spread of pollution remains only local and can be kept under control. Waters flowing in isolated pit bottom area are pumped out and after purification used for technological needs. In 1993-1995 about 150 thousand $\text{m}^3 \text{yr}^{-1}$ of mine water was used in this way, mainly in the circulation cycles of cooling water.

After the stopping of the pumps, the mining galleries were filled by water in approximately 7-8 months from south to north. The maximum rise of water level (41.5 m abs.) fully corresponded to the mine closing (liquidation) design [3].

The water level in the closed mine is presently regulated by an outflow through the ditches system into the Purtse River. The parameters of water outflow largely depend on the meteorological conditions in this region and the minimum and maximum parameters may differ about 8-10 times. The

largest quantities (4000-8000 m³ h⁻¹) usually occur in April-May, when a strong infiltration of rain and thaw waters underground takes place.

The Dynamics of Physico-Chemical Composition of Mine Water Outflow

Annual average contents of sulfates, chlorides, Ca, Mg, Na and K and total hardness of mine water flowing out from closed *Kiviõli* mine in 1988-1996 are presented in Table 1, the results of mathematical-statistical analysis of these parameters in Table 2.

From Table 1 it appears that in comparison with the year 1988, the content of sulfates in water and its total hardness are decreased 3 times, content of chlorides and Na + K about twice. Total content of Ca and Mg within the same period has also decreased 3 times. The calculated correlation coefficients well prove the veracity and interdependence of obtained data (Table 2).

Within the limits of values indicated in Table 1 (the contents of anions-cations from 1988 until 1996), the contents of sulfates, chlorides, Ca, Mg, Na, and K in mine water can be easily calculated by linear regression equations $y = a + bx$, whose coefficients a and b are computed by regression analysis of annual average values (Table 2).

Data concerning the concentration of phosphates, nitrates, iron, volatile phenols, oil products and COD in mine water were also analysed for the period 1988-1996. In their contents some essential changes have also taken place.

If in 1991-1992 the content of phosphates in mine water did not rise above 0.04 mg/L, then during the following years (1993-1996) their content fell practically to zero level (below 0.001 mg/L). The content of iron in 1988-1996 remained practically on the same level, fluctuating within the range of 0.08-0.12 mg/L. Content of nitrates remained within an interval of 0.20-3.80 mg/L during the examination period, reaching its average peak in 1993 with 2.99 mg/L. Nitrates accumulate in mine water with inflowing rain and snow waters and are in connection with farming, primarily due to a negligent treatment with manure and nitrate fertilizers.

Table 1. Annual Average Physico-Chemical Parameters of Mine Water Flowing Out from Closed *Kiviõli* Mine during the Period of 1988-1996

| Year | Average contents, mg/L | | | | | | |
|------|------------------------|-----------|----------------------------|-----|------|---------|--------|
| | Sulfates | Chlorides | Total hardness, mg-equiv/L | Ca | Mg | Ca + Mg | Na + K |
| 1988 | 882 | 53.9 | 29.80 | 459 | 83.9 | 542.9 | 39.9 |
| 1989 | 742 | 35.2 | 21.00 | 325 | 58.3 | 383.3 | 29.1 |
| 1991 | 415 | 36.7 | 13.85 | 205 | 43.8 | 248.8 | 25.8 |
| 1992 | 354 | 32.5 | 12.43 | 184 | 39.5 | 223.5 | 26.4 |
| 1993 | 295 | 33.0 | 11.78 | 165 | 42.9 | 207.9 | 26.9 |
| 1994 | 298 | 29.8 | 11.90 | 172 | 40.1 | 212.1 | 26.0 |
| 1995 | 296 | 33.2 | 10.35 | 125 | 49.8 | 174.8 | 22.5 |
| 1996 | 285 | 30.3 | 9.67 | 137 | 42.1 | 179.1 | 21.8 |

Table 2. The Results of Mathematical-Statistical Analysis of Annual Average Physico-Chemical Parameters of Mine Water Flowing Out

| Paired parameters (x, y) | Standard deviation | | Correlation coefficient, $r(x,y)$ | Coefficients of regression equation | |
|-----------------------------------|--------------------|----------|-----------------------------------|-------------------------------------|---------|
| | $s(x)$ | $s(y)$ | | a | b |
| Sulfates - total hardness | 233.0735 | 6.8962 | 0.9778 | 2.1976 | 0.0289 |
| Sulfates - chlorides | 233.0735 | 7.7470 | 0.8367 | 23.1744 | 0.0278 |
| Total hardness - (Ca + Mg) | 6.8962 | 127.8607 | 0.9993 | -8.1780 | 18.5281 |
| (Ca + Mg) - chlorides | 127.8607 | 7.7470 | 0.9053 | 20.6794 | 0.0549 |
| Sulfates - (Ca+Mg) | 233.0735 | 127.8607 | 0.9794 | 31.9768 | 0.5373 |
| (Na + K) - (sulfates + chlorides) | 5.6087 | 239.5933 | 0.8817 | -546.8562 | 37.6669 |

It is important to note that the content of volatile phenols and oil products in mine water have also fallen to zero level (below 0.001 mg/L) already at the outset of 1991. This fact indicates that the phenol and oil pollution originating from pit bottom located under the territory of Kiviõli OSP does not leak out any longer to the southern mining galleries. Before the closure of the mine the contents of volatile phenols and oil products in mine water pumped out reached respectively 0.250 and 0.450 mg/L [1]. This pollution continuously spreaded into the Purtse River first and from there flowed to the Gulf of Finland.

The value of COD has also fallen noticeably: if its maximum value amounted 28.6 mg/L in 1991, then during the period of 1995-1996 the maximum figure did not exceed 18.2 mg/L. Supposedly the diminishing of COD value will continue during the following years as well.

On these grounds we may conclude that the mine water flowing out at the present time into the Purtse River does not represent a danger in terms of river water quality: the composition parameters are stabilized, and water is practically pure, having good potential for realization of different using variants (even as potable water). The design solution applied for the mine closing has proved itself to be effective enough.

Hydrochemical and Geochemical Processes in Changed Underground Environment

There is no doubt that the factors that essentially influence the physico-chemical composition of underground water (mine water) before oil shale mining, during the mining period and after closing the mine are inevitably different and function with a different action mechanism and efficiency. Table 3 presents the list of these main factors in generalized form and shows their effects according to underground situations.

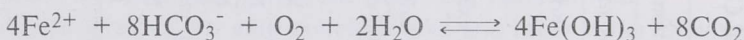
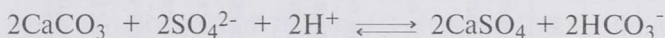
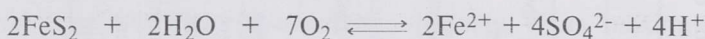
Table 3. The Factors Affecting the Physico-Chemical Composition of Underground Water (Mine Water)

| Factors | Situation | | |
|--|--------------------------------|--|---|
| | Before mining | In mining period | After closing the mine |
| Nature of water underground moving | Slow, laminar flow | Turbulent flow | Predominantly turbulent flow |
| Mixing of different water layers and its interaction | Minimum | Very intensive | Intensive |
| Mixing with rain-water and snow water (from above) | Non-existent or rather weak | Excellent | Excellent |
| Contact of underground water (mine water) and oil shale with aerial oxygen | Non-existent or rather weak | Excellent (ventilating air + inflowing water from above) | Minimum (only inflowing water from above) |
| Oxidation of pyrite, genesis of sulfates, oxidation of other Fe-compounds | Non-existent or passing slowly | Occurring intensively | Passing to a less extent |
| Contact of underground environment with blasting gases | Non-existent | Excellent | Lacking |
| Changes of temperature | Non-existent | Taking place seasonally | Taking place seasonally |
| Pollution with oil products and phenols | Non-existent | Taking place noticeably | Diminishing step by step up to nought |
| Contact of underground environment with CO ₂ | Non-existent or minimum | Excellent | To an essential extent continuously |
| Bacterial processes (sulfate bacteria) | Non-existent | Present | Present |
| Influence of agricultural pollution | Insignificant | Noticeable | Noticeable |

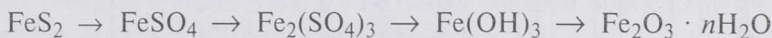
From Table 3 it becomes evident that in the course of mine foundation, its exploitation and later closure the natural hydrogeochemical connection between water layers formed during millenniums is damaged. In this area, some irreversible qualitative and quantitative transformations in underground water composition will occur unavoidably. All this results in forming a new situation that can be described as hydrogeochemical anomaly [6, 7].

After closing the *Kiviõli* mine a natural-technogenic equilibrium began to form itself in the observation area. During the period that followed after the closure, the direction of the groundwater movement changed, increasing the flow gradient of moving groundwater and evolving a new total balance of groundwater and surface water fluxes. As there is no technogenic pumping out, the groundwaters and surface waters have made up a new unitary and hydraulically connected system in closed mine area, whereby the velocity of water flowing out from flooded mining galleries is strongly affected by meteorological conditions of a concrete year (rains, thickness of snow layer, freezing depth of ground).

With atmospheric precipitations (i.e. rain and snow waters), a considerable amount of carbon dioxide (CO₂) and oxygen (O₂) permeates underground. In contact with oil shale, carbonate rocks, and groundwater, they lead to various chemical reactions. Let us observe some of them. First of all there are reactions with a participation of pyrite (FeS₂) originating from oil shale:



Pyrite is transformed in the oxidation zone according to a following scheme:

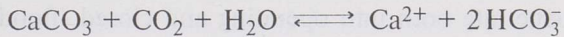


As a result of the pyrite oxidation, the ions of Mg²⁺, Ca²⁺, Cl⁻ and SO₄²⁻ get into the water. This process is particularly intensive in case of oil shale mining accompanied by a continuous outpumping of mine water. The pyrite occurring in oil shale is well accessible to oxygen, as the statical conditions in water regime are practically non-existent. The nitrogen dioxide (NO₂) existing in blasting gases is also a strong oxidant.

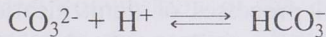
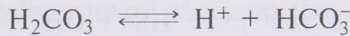
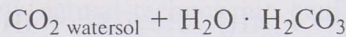
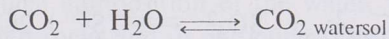
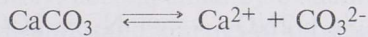
After overflowing the mine, the aeration zone diminishes considerably and the oxidation velocity of pyrite decelerates which is precisely expressed by abatement of sulfate and other ions contents in outflowing water (Table 1). Due to the effect of HCO₃⁻ ions and oxygen, an intensive

oxidation of natural bivalent iron to trivalent also occurs, causing a characteristic reddish-brown colouring of water. This reaction results in an unpleasant water colour in the shallow potable water wells which ordinarily receive the feeding from mine water after flooding the mine.

The second group of reactions is associated with dissolution of CaCO_3 by the action of CO_2 :



This reaction consists of the following subreactions:



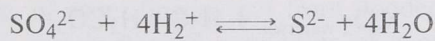
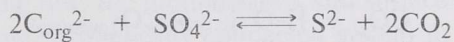
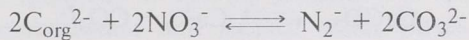
If the CO_2 content in water somewhat rises, then the amount of H^+ ions also increases. Some H^+ ions react in turn with CO_3^{2-} with simultaneous equalizing of pH. If pH lies within the range of 7.5-8.5, then the bicarbonate ion is dominating in water. The pH of the water pumped out from the mine lay within this interval, being at the present time also identical for the water outflowing from the closed *Kiviõli* mine.

As a result of dissolving CaCO_3 and dissociation processes of bicarbonate ions, the so-called latent stage in system $\text{CO}_2\text{-H}_2\text{O-CaCO}_3$ is formed: solution is in the state of metastability or in the supersaturated condition with regard to CaCO_3 , essentially influenced by ions of Mg^{2+} and SO_4^{2-} [8]. With the fall of these contents a partial precipitation of CaCO_3 occurs. Such hydrochemical processes are continuously taking place underground, both in the operating mines as well as in the closed ones.

Due to the effect of CO_2 dissolved in water, the mobility of such elements as Fe, Mn, Cu, Mg, Ca, Co, Ni, Ba, Zn, Cd and Sr changes steeply, whereas the bicarbonates of these are better soluble in water. The CO_2 effect is contrary to Na and K (bicarbonates are less soluble in water than hydroxides) and also to Cr, V, Al, Ti and Pb (as by the effect of CO_2 and water the insoluble hydroxides appear) [8]. These processes are rather complicated but also vital for us. They need further detailed investigations because the Estonian oil shale also contains a number of heavy metals and microelements [9]. As a result of hydrochemical processes, those elements move from oil shale into the mine water creating a new anthropogenic

background with regard to metals, while the background concentrations of metals in the mine water largely depend on the CO_2 content in water, thus upon the dynamics of pH. For example, an explanation about the chemism of transforming selenium compounds by the effect of mine water is needed, whereas Se occurs in the composition of oil shale together with sulfur compounds.

Organic carbon and different bacteria, as well as microorganisms can most easily penetrate both into operating and closed (flooded) mines with intruding water from above. As a result, the following reactions will occur underground:



Such are some typical processes of denitrification and desulfurization that begin with intrusion of organic contamination (for example humic acids, carbohydrates) into the flooded mine. As a result of these reactions, the ionic composition of outflowing water and pH, may also change. The latter will rise due to the hydrolysis of S^{2-} ions. The biogenic CO_2 will emerge, accompanied by a different hydrochemical anomaly (with organic extraction), causing the retention of the pollution aureole during a long time [8]. In such reactions, iron performs the role of catalyst, promoting the transition of oxygen to the organic carbon. Under certain conditions, the carbon of oil shale organic matter (kerogen) can participate in these reactions with a resulting generation of CO_2 . Simultaneously the biological oxidation of pyrite included in the composition of oil shale may occur [10], but only under rather specific conditions (pH < 3 in case of thermophilic or mesophilic microorganisms). Such conditions are presently non-existent in the underground environment.

From the above it becomes evident what kind of hazards are still connected with continuous influx of organic pollution into mine water, especially as a result of farming activity (organic manures, the products of decomposition of plants etc.). On the former Kiviõli mining field the corresponding conditions are favourable, if to take into consideration the existence of hundreds of badly closed geological boreholes. The smell of hydrogen sulfide (H_2S) can be sometimes felt in mine water outflowing from the mining galleries during the second half of summer evidently due to this reason. The sulfides, however, will be relatively quickly oxidized into thiosulfates by the effect of air oxygen.

Thus, the area of the closed *Kiviõli* mine is rather susceptible with respect to agrarian organic pollution since the overburden rocks are not particularly thick and even these are partially deformed and damaged, forming so-called hydrogeological windows.

Conclusions

In the closed and flooded *Kiviõli* mine both heterogenous and homogenous physico-chemical, geochemical and biological processes are taking place continuously, accompanied by oxidation, cation exchange and hydrolysis. The intensiveness and kinetics of those processes largely depend on the physico-chemical composition of the water, filtrating underground through the overburden rocks and in particular on the content of CO_2 and O_2 . In this region new natural-technogenic equilibrium and piezometric regime are formed, as a result of a total effect of geomechanical, hydrogeomechanical and hydrotechnical processes that occurred simultaneously during the oil shale mining.

The physico-chemical composition of the outflowing mine water has stabilized with a decrease in the content of main components up to 2-3 times. The oil and phenolic pollution have been flushed out and currently reach the zero level. The outflowing water does not represent an essential risk for the quality of the Purtse River water any more. The contents of sulfates, chlorides, Ca, Mg, Na and K in the mine water are mutually well-determinable by linear regression equations which are deduced by statistical calculations on the ground of experimental analyses data.

An ecological monitoring of outflowing mine water is necessary, particularly during the summer period, when the chances of infiltration caused by the tillage pollution (organic and anorganic fertilizers) grow. More detailed investigations concerning the content dynamics of heavy metals and microelements are necessary, whereas their mobility within the system oil shale strata-underground water is conditioned by specific properties of infiltrating underground waters (in the first place by the content of CO_2 and O_2). The latter may also change the thermal regime of underground water flux, activating thereby the exothermic hydration processes.

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