

EMISSION OF VOLATILE PHENOLS FROM STABILIZATION PONDS OF OIL SHALE ASH DUMP LEACHATE

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The Viru Chemistry Group AS oil shale processing plant at the town of Kohtla-Järve in the North-East of Estonia uses stabilization ponds with a total area of 16.3 ha for stabilization of pH and concentration of phenols in the leachate from semicoke dumps. At pH ~ 11 and a background concentration of phenols ca $5 \mu\text{g m}^{-3}$ in the atmosphere over the water surface, the emission of phenols from leachate into the air remains minimal, while the maximum emission intensity of phenols equals 0.0035 g s^{-1} (by an annual quantity about 0.07 t) if the water pH decreases down to 9.4. The total annual emission of phenols during the course of water from stabilization ponds via a special channel into the Kohtla and Purtse rivers and finally into the Gulf of Finland equals ca 12 t. The formulas are elaborated for calculation of emission intensity and annually emitted amount of phenols into the air, depending on leachate temperature and pH, as well as on phenols concentration in the water and their background level in the air.

Introduction

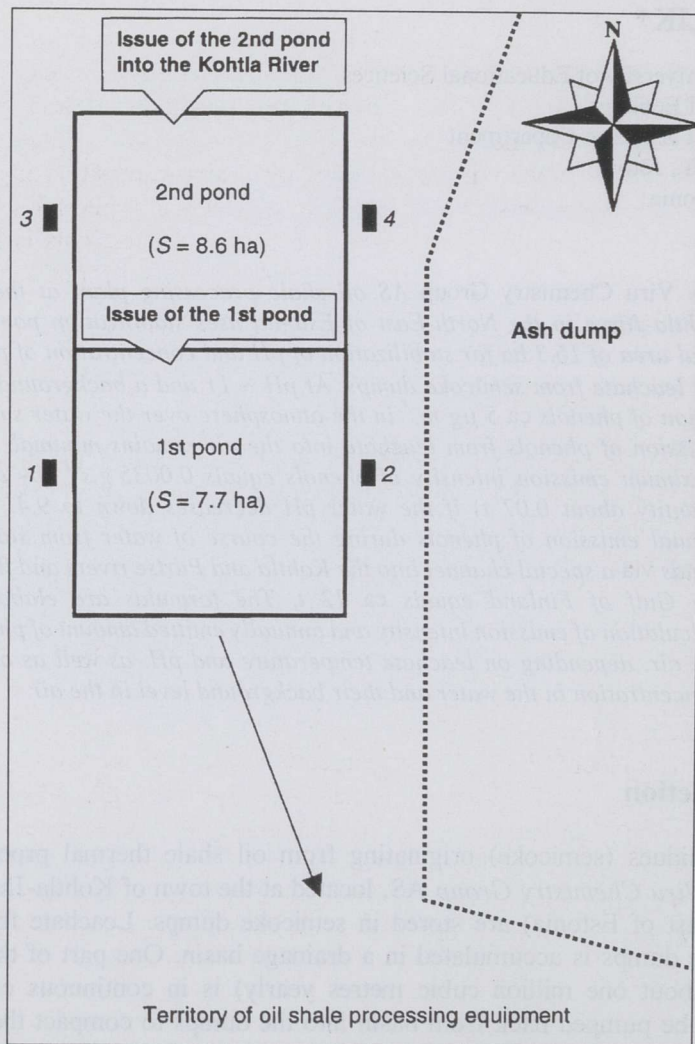
Solid residues (semicoke) originating from oil shale thermal processing in retorts (Viru Chemistry Group AS, located at the town of Kohtla-Järve in the North-East of Estonia) are stored in semicoke dumps. Leachate from those semicoke dumps is accumulated in a drainage basin. One part of this wastewater (about one million cubic metres yearly) is in continuous circulation and will be pumped back from basin into the dumps to compact the ash and semicoke. In order to prevent the choking of pipelines (due to fall out of mineral salts in strong alkaline solutions) acid tar is added into water basin.

As a result of precipitation and additional amounts of technological wastewater pumped into dumps, a remainder amount of leachate is generated

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which until recently was conveyed from drainage basin without further treatment *via* a special channel system into the Kohtla and Purtse rivers and finally into the Gulf of Finland.

Thus a serious pollution problem arises. According to the statistics of *Viru Chemistry Group AS* in 1993–1997, the influx of volatile phenols into the Kohtla River totalled about 24 t (*ca* 660,000 m³ of leachate) yearly, while concentration of volatile phenols in leachate during this period remained within the ranges of 1–206 mg l⁻¹ (average value 41 mg l⁻¹) and pH 1.6–12.6 (9.4).



Scheme of location of ash dump leachate ponds.

1-4 – measurement points of phenol concentration in the air

Since the spring of 1997 the leachate from semicoke dumps has been accumulated in special stabilization ponds, with a prime purpose to stabilise the pollutant concentration and other physical and chemical properties of wastewater. This is important in order to prevent very high pollution loads on natural water bodies, as well as for preparation of leachate before its direction to the wastewater treatment plant. There are two stabilization ponds located side by side, with areas 7.7 ha and 8.6 ha, respectively (see the Scheme). The walls and bottom of ponds are built from oil shale ash (from power plant boilers using oil shale) and the maximum level of water may rise up to 2 m.

Thus, the stabilization ponds represent an artificial lake with a total area of 16.3 ha within the borders of the town of Kohtla-Järve, which can be defined as a new source of pollutant emission into the atmosphere. The main pollutants are volatile phenols – phenol (hydroxybenzene) and its methyl derivatives (2-, 3-, and 4-methylphenols).

This paper deals with investigation of emission intensity per time unit and total annual amounts of volatile phenols, which can be emitted into the atmosphere from the above-mentioned stabilization ponds. This is important in order to determine the role of ponds in formation of all-round air pollution level in terms of phenols.

Equipment and Methods

For analysing the concentration of volatile phenols in the atmospheric air in region of the ponds, a method based on the reaction of phenols with paranitroaniline was used [1]. The content of phenols in water was ascertained spectrometrically using the reaction with 4-aminoantipyrine [2].

To investigate the maximum emission intensity of volatile phenols, a laboratory pilot model of stabilization ponds was used. This model consists of cylindrical glass dish with an interior diameter of 22 cm and height of 6 cm. The dish was filled up to 3/4 with leachate previously treated with sulfuric acid in order to fix the value of pH within the range of 5.0–5.3. An air current (velocity 3 m s^{-1}) was directed over the water layer with simultaneous imitation of light waves in the water layer with the aid of vibration. Duration of the experiment, pH, water temperature, and concentration of phenols in the water before and after experiment were fixed. The results of laboratory experiments were used, first of all, for calculation of air pollution loads by computer imitation program IMIT based on a semi-empirical method [3, 4].

Theoretical Part

The circulating water contacting with ash and semicoke dissolves organic and inorganic ash components, including phenols. From soluble total

phenols only volatile compounds emit into the air – mainly phenol (hydroxybenzene) and methylphenols. The content of ethyl- and dimethylphenols in the air is negligible. Since 3-methylphenol dominates among methylphenols [5], only phenol and 3-methylphenol are henceforth studied in detail. Phenols as weak acids have dissociation constants between 10^{-11} – 10^{-10} (Table 1).

Table 1. Dissociation Constants of Phenols [6]

Component	K_a	pK_a
Phenol	$1.0 \cdot 10^{-10}$	10.00
2-Methylphenol	$5.2 \cdot 10^{-11}$	10.29
3-Methylphenol	$8.1 \cdot 10^{-11}$	10.09
4-Methylphenol	$5.5 \cdot 10^{-11}$	10.26
2,4-Dimethylphenol	$6.46 \cdot 10^{-11}$	10.19
2,4,6-Trimethylphenol	$1.6 \cdot 10^{-11}$	10.80
Thiophenol	$3.7 \cdot 10^{-10}$	9.43
Resorcinol	$3.6 \cdot 10^{-10}$	9.44

Table 2. Dissociation Degree of Phenols in Water (α) Depending on pH

pH	Phenol	3-Methylphenol	pH	Phenol	3-Methylphenol
5.0	0.00001	0.00001	10.2	0.616	0.565
6.0	0.0001	0.0001	10.3	0.669	0.621
7.0	0.001	0.001	10.4	0.717	0.673
7.5	0.003	0.003	10.5	0.762	0.721
8.0	0.010	0.008	10.6	0.801	0.766
8.1	0.013	0.010	10.7	0.835	0.804
8.2	0.016	0.013	10.8	0.864	0.838
8.3	0.020	0.016	10.9	0.889	0.867
8.4	0.025	0.020	11.0	0.910	0.891
8.5	0.031	0.025	11.1	0.927	0.912
8.6	0.039	0.032	11.2	0.941	0.929
8.7	0.048	0.039	11.3	0.953	0.942
8.8	0.061	0.049	11.4	0.962	0.954
8.9	0.074	0.061	11.5	0.970	0.963
9.0	0.092	0.076	11.6	0.976	0.970
9.1	0.113	0.094	11.7	0.981	0.976
9.2	0.138	0.115	11.8	0.985	0.981
9.3	0.168	0.141	11.9	0.988	0.985
9.4	0.202	0.171	12.0	0.990	0.988
9.5	0.242	0.206	12.1	0.992	0.990
9.6	0.288	0.246	12.2	0.994	0.992
9.7	0.336	0.291	12.3	0.995	0.994
9.8	0.389	0.341	12.4	0.996	0.995
9.9	0.445	0.395	12.5	0.997	0.996
10.0	0.503	0.451	13.0	0.999	0.999
10.1	0.560	0.508	14.0	0.9999	0.9999

Table 3. The Saturated Vapour Pressure p_f of Phenols and Their Equilibrium Concentration c_0 over the Waters under Standard Conditions (Concentration of Phenols in Water 100 mg l^{-1} , $\text{pH} < 5$) Depending on Temperature

Temperature, °C	Phenol		3-Methylphenol	
	p_f , mm Hg	c_0 , $\mu\text{g m}^{-3}$	p_f , mm Hg	c_0 , $\mu\text{g m}^{-3}$
0	0.079	8.3	0.015	1.6
1	0.086	9.1	0.017	1.8
2	0.094	9.9	0.018	1.9
3	0.102	10.8	0.020	2.1
4	0.111	11.7	0.022	2.3
5	0.120	12.7	0.024	2.6
6	0.131	13.8	0.027	2.8
7	0.142	15.0	0.029	3.1
8	0.154	16.2	0.032	3.4
9	0.167	17.6	0.035	3.7
10	0.180	19.0	0.039	4.1
11	0.195	20.6	0.042	4.5
12	0.211	22.3	0.046	4.9
13	0.228	24.0	0.050	5.3
14	0.247	26.0	0.055	5.8
15	0.266	28.1	0.060	6.4
16	0.288	30.4	0.066	6.9
17	0.310	32.7	0.072	7.6
18	0.335	35.3	0.078	8.2
19	0.361	38.1	0.085	9.0
20	0.388	40.9	0.092	9.7
21	0.418	44.1	0.100	10.6
22	0.450	47.5	0.109	11.5
23	0.484	51.0	0.118	12.5
24	0.520	54.9	0.128	13.6
25	0.559	59.0	0.139	14.7
26	0.600	63.3	0.151	16.0
27	0.645	68.0	0.164	17.3
28	0.692	72.9	0.177	18.7
29	0.742	78.2	0.192	20.3

For diluted solution the dissociation constant of phenol (hydroxybenzene) is described by the following equation:

$$K_a = \frac{[\text{H}^+][\text{C}_6\text{H}_5\text{O}^-]}{[\text{C}_6\text{H}_5\text{OH}]} \quad (1)$$

where $[\text{H}^+]$, $[\text{C}_6\text{H}_5\text{O}^-]$ and $[\text{C}_6\text{H}_5\text{OH}]$ are the concentrations of the corresponding ions and undissociated molecules of phenol.

The Equation (1) may be expressed as

$$\text{p}K_a = \text{p}H - \frac{[\text{C}_6\text{H}_5\text{O}^-]}{[\text{C}_6\text{H}_5\text{OH}]} \quad (2)$$

On the basis of this expression the dissociation degree α of phenol and 3-methylphenol depending on pH of wastewater was calculated (Table 2). The saturated vapour pressure p_f of phenols (Table 3) depending on the temperature was calculated according to the data published in literature [7], using the regression equation:

$$\log P = a + \frac{b}{T} \quad (3)$$

According to the Raoult's law the saturated vapour pressure of a component over the solution is directly proportional to its mole fraction [8]. By using this law the equilibrium concentrations c_0 of phenol and 3-methylphenol over the waters depending on temperature were also calculated (Table 3).

The maximum concentration of phenols over the waters (c_a , $\mu\text{g m}^{-3}$) and the emission intensity from the surface of ponds (I_f , g s^{-1}) may be calculated by the following formulas:

$$c_a = \frac{c_0 \cdot c_w \cdot (100 - \alpha)}{100} \quad (4)$$

$$I_f = I_0 \cdot \frac{c_w \cdot p_f \cdot (100 - \alpha) \left(1 - \frac{c_f}{c_a}\right)}{38.80} \quad (5)$$

where c_0 – equilibrium concentration of phenol over the ponds, $\mu\text{g m}^{-3}$ (Table 3);

c_w – concentration of phenol in water, mg l^{-1} ;

α – dissociation degree of phenol;

p_f – equilibrium pressure of saturated phenol vapour over the solution, mm Hg (Table 3);

c_f – background concentration of phenol in air, $\mu\text{g m}^{-3}$;

I_0 – emission from ponds under standard conditions, g s^{-1} .

Under standard conditions the concentration of phenols in water is equal to 100 mg l^{-1} , water temperature – $20 \text{ }^\circ\text{C}$ and pH – 5.0 or less.

Results and Discussion

Characterisation of Leachate in the Ponds

In the period of June–October 1997 recently finished ponds were filled with leachate. During this time the wastewater was pumped into the ponds and an overflow from the ponds into the Kohtla River did not take place. The pH value of wastewater pumped into ponds (Table 4) varied between 1.5–11.8 (average 9.6) and the concentration of volatile phenols between $8\text{--}82 \text{ mg l}^{-1}$ (average 46 mg l^{-1}).

Table 4. Characterization of Drainage Leachate Directed from the Ash Dump to the Ponds during Their Filling with Wastewater (July–September 1997)

Parameters	July			August			September			Average
	Minimum	Maximum	Average	Minimum	Maximum	Average	Minimum	Maximum	Average	
pH	1.5	11.4	8.0	4.3	11.6	9,5	8.9	11.8	10.7	9.6
Concentration, mg l ⁻¹ :										
Volatile phenols	10	82	58	8	80	46	14	53	34	46
Total phenols	80	110	94	35	93	63	62	84	73	77

Table 5. Characterization of Drainage Leachate Discharged from the Ponds to the Kohtla River on the Ground of Average Monthly Data (October 1997 – April 1998)

Year	Month	Volume of water, m ³ per month	pH	Phenols, mg l ⁻¹	
				Volatile	Total
1997	October	79,600	10.8	19	48
1997	November	158,400	12.2	35	57
1997	December	5,100	12.6	43	70
1998	January	21,500	12.1	50	92
1998	February	61,455	9.1	58	102
1998	March	23,570	10.3	59	107
1998	April	64,660	11.2	46	85
Average		59,184	11.2	44	80

The overflow from stabilization ponds into the Kohtla River occurred for the first time in October 1997. Normal exploitation of the ponds continued until June 1998, when the ponds were emptied for repair. During this period the average characteristics of water influx from ponds into the Kohtla River were the following (Table 5): pH = 11.2, concentration of volatile phenols 44 mg l⁻¹ and total phenols 80 mg l⁻¹.

From Tables 4 and 5 we can see that in the drainage leachate discharged from the ponds to the Kohtla River the pH value was essentially rising (from 9.6 to the level of 11.2), in comparison with leachate directed to the ponds from the semicoke dumps. At the same time the changes in concentration of phenols were not significant and remained practically at the same level (by inflow 46 and by issue 44 mg l⁻¹). The increase in leachate pH is probably the result of the contact of water with strongly alkaline construction material of ponds – oil shale ash.

Table 6. Characterization of Different Leachate Samples (January–April 1998)

Date	pH		Volatile phenols, mg l ⁻¹	
	Issue of the 1st pond	Issue of the 2nd pond	Issue of the 1st pond	Issue of the 2nd pond
14.01.98	12.8	12.7	53	52
26.01.98	12.4	12.1	40	33
06.02.98	12.0	12.1	52	52
09.02.98	12.1	12.0	41	38
05.03.98	10.9	11.0	41	44
11.03.98	11.6	11.7	34	36
01.04.98	11.8	11.9	40	40
06.04.98	12.2	12.3	50	52
16.04.98	12.4	12.3	50	32
Average	12.0	12.0	45	42

Concentrations of volatile phenols in leachate measured at the issues from the first and second ponds (see Scheme) also characterize a relatively low emission intensity of phenols (Table 6). The latter is explained by the high pH value of leachate (*ca* 12.0), in which case phenols are nearly completely dissociated ($\alpha \approx 0.99$) into ions.

Concentrations of Phenols in the Air

The maximum concentration of phenols in the air, caused by its volatilization from the pond surface (c_a), depends on the concentration of phenols in water, water pH and temperature. In addition to the above-mentioned factors, the emission intensity (I_f) is very sensitive to the changes in the phenol background concentration (c_f) in the air.

To determine the values of c_f , investigations of atmospheric air composition in the region of the ponds were carried out. Table 7 shows that the concentration of phenols in the air between the ponds equalled 21–50 $\mu\text{g m}^{-3}$ during the ice-free period, whereby the highest concentration was

Table 7. Concentration of Phenols in the Air over the Territory between the Ponds under Different Meteorological Conditions (April–July 1998)

Date	Wind direction	Wind velocity, m s ⁻¹	Air temperature, °C	Concentration, $\mu\text{g m}^{-3}$
16.04.98* ¹	SO	5	6.2	10
22.04.98	NO	3	7.4	21
04.05.98	NO	3	14.3	34
10.06.98	S	6	21.0	50
26.06.98* ²	NW	4	17.0	6
02.07.98* ²	NO	3	17.0	4
06.07.98* ²	NO	4	19.4	5

Note: *¹ frozen ponds; *² empty ponds.

fixed in the case of southerly wind blowing from the direction of oil shale processing plant. Such a result is to be expected because in the territory of this plant also other emission sources of phenols are located. In the case of southerly wind, frozen ponds (phenols volatilization from the pond surface is absent), and the air temperature 6.2 °C, the content of phenols in the atmosphere was $10 \mu\text{g m}^{-3}$, which can be considered the average background concentration (c_f) of phenols in the case of winds blowing from the direction of oil shale processing plant (see the Scheme). In the case of northern wind (winds blowing from natural areas) and empty ponds, a background concentration of $5 \mu\text{g m}^{-3}$ was established. Table 8 presents the phenol concentrations measured in front and after the ponds in August 1997.

Using the experimental data from Table 9 as input data and assuming that the concentration of phenol in the air over the ponds should not exceed its equilibrium concentration c_0 (Table 3), the emission intensity from the surface of ponds I_0 was calculated (Eq. (5)) by application the IMIT program [3]. Presuming that $\text{pH} = 5$, $c_w = 100 \text{ mg l}^{-1}$, water temperature = 20 °C, and not considering the background concentration of phenol ($c_f = 0$), the calculated emission intensity from the surface of ponds under standard conditions was obtained: $I_0 = 0.091 \pm 0.014 \text{ g s}^{-1}$.

Operating with the concentration of phenol in leachate ($c_w = 41 \text{ mg l}^{-1}$ as the long-time average concentration) and with the temperature of water in summer days ($t = 21 \text{ °C}$), as well as with above-mentioned background concentrations, the values of c_a and I_f were calculated by using Eq. (4) and Eq. (5) depending on pH and c_f values.

Table 8. Measurement Conditions and Phenol Concentration in the Air in Front and After the Ponds

Date	Wind parameters		Air temperature, °C	Point of measurement (see Scheme)	Water temperature, °C	Concentration of phenols, $\mu\text{g m}^{-3}$
	Direction	Velocity, m s^{-1}				
14.08.97	WNW	10.0	19.0	1	15,5	10
				2	16,5	7
15.08.97	NW	6,5	21.3	1	23,5	7
				2	12,5	5
19.08.97	SW	1.1	19.3	1	16.5	0
				2	16.0	4
20.08.97	SW	1.6	22.6	1	18.0	19
				4	17.0	22
21.08.97	W	1.3	20.2	3	19.5	12
				2	20.0	12
22.08.97	W	1.2	20.4	3	19.5	8
				2	20.5	13
26.08.97	SW	1.3	23.0	1	19.0	8
				4	19.5	18
27.08.97	SW	2.0	22.9	1	20.0	9
				4	19.0	24

Table 9. Experimental Conditions and the Maximum Emission Intensity of Phenol

Conditions	Experiment 1 (15.05.1998)	Experiment 2 (11.06.1998)
Volume of wastewater, l	1.5	1.5
Diameter of experimental vessel, cm	22	22
Duration of experiment, h	5	28
Temperature of wastewater, °C:		
Minimum	14	19
Maximum	16	22
Average	15	21
Water pH	5.3	5.0
Air velocity above vessel, m s ⁻¹	3	3
Concentration of phenol in water, mg l ⁻¹ :		
At the beginning	46	24
At the end	43	16
Average	44.5	20
Emission intensity I_f of phenol, mg m ⁻² h ⁻¹	77.6	52.3

Table 10. Maximum Concentration in Air (c_a) and Emission Intensity (I_f) of Phenol depending on Wastewater pH and Phenol Background Concentration of (c_f , µg m⁻³)

pH	c_a , µg m ⁻³	I_f , g s ⁻¹		
		$c_f = 0$	$c_f = 5$	$c_f = 10$
7.0	18.1	0.0961	0.0695	0.0430
7.5	18.0	0.0959	0.0692	0.0426
8.0	17.9	0.0952	0.0686	0.0420
8.5	17.5	0.0932	0.0666	0.0399
9.0	16.4	0.0873	0.0607	0.0341
9.5	13.7	0.0729	0.0463	0.0197
10.0	9.0	0.0478	0.0212	0.0000
10.5	4.3	0.0229	0.0000	0.0000
11.0	1.6	0.0087	0.0000	0.0000
11.5	0.5	0.0029	0.0000	0.0000
12.0	0.2	0.0010	0.0000	0.0000

The results of calculations (Table 10) show that the concentration of phenol in the air caused by ponds may vary within the interval of 0.2–18.1 µg m⁻³. An emission of phenols into the atmosphere occurs only if $c_a > c_f$; otherwise the absorption of phenols from the atmosphere into waters takes place. Since during the current exploitation of the ponds the value of pH varied predominantly within the range of 11–12 (Tables 5 and 6), even a minimum background concentration ($c_f = 5$) practically suppresses the emission of phenols (Table 10). The results of measuring the concentration

of phenols in the air in front and after the ponds (Table 8) show a moderate rising of phenol concentration in the air while crossing the ponds: averagely $4 \mu\text{g m}^{-3}$, which is in accordance with the calculated data.

Emission Intensity and Annual Emission of Phenols

By calculation of the monthly average concentration and total annual emission of phenols we proceeded from the monthly average air temperature in Estonia [9]; the concentration of phenols in the leachate was supposed to be equal to 41 mg l^{-1} . Since by $\text{pH} \sim 11.2$ the emission of phenols is practically non-existent, the value $\text{pH} = 9.4$ was used in calculations, which is characteristic for a situation where the construction material of ponds will not cause the increase in pH, e.g. as a result of pond exploitation during several years. Calculations were carried out for the ice-free season first without any respect to the background concentration ($c_f = 0$) and secondly by the background concentration of volatile phenols $c_f = 5 \mu\text{g m}^{-3}$ (Table 11).

The above calculations were made assuming that the volatile phenols consist only of the first member of homologous series of monohydric phenols – of hydroxybenzene (phenol), though there exists also a considerable amount of methylphenols both in air and water. Because the component content of volatile phenols is not exactly known, it was supposed that the concentration ratio phenol: methylphenols in leachate equals 3 : 2 and in air – 4 : 1. The results of that calculation are presented in Table 12. In the case of the background concentration $c_f = 5 \mu\text{g m}^{-3}$, the total maximum emission of phenols equals 0.0035 g s^{-1} and annual quantity approximately 0.07 t. Since the annual emission from the territory of *Viru Chemistry Group AS* totals 5 t, the share of ponds forms a little more than 1 %.

Thus, the small impact of ponds upon the pollution level of surrounding environment can be easily explained. However, if in the future the neutralization occurs immediately in the ponds, the emission of phenols also increases. In that case the maximum intensity of emission may increase as

Table 11. Monthly Average Emission Intensity (I_k) and Total Emission (q) of Phenols at the Phenol Concentration in the Leachate 41 mg l^{-1} , $\text{pH} = 9.4$ and Different c_f ($\mu\text{g m}^{-3}$)

Month	Temperature, °C	c_a , $\mu\text{g m}^{-3}$	I_k , g s^{-1}		q , ton per month	
			$c_f = 0$	$c_f = 5$	$c_f = 0$	$c_f = 5$
April	4.0	3.8	0.009	0.0000	0.022	0.000
May	9.6	6.0	0.013	0.0023	0.036	0.006
June	14.4	8.8	0.019	0.0083	0.050	0.022
July	17.1	10.8	0.024	0.0129	0.064	0.035
August	15.2	9.4	0.021	0.0096	0.055	0.026
September	10.4	6.4	0.014	0.0031	0.037	0.008
October	4.5	4.0	0.009	0.0000	0.024	0.000
Total					0.288	0.097

high as 0.09 g s^{-1} , considering that the concentration of volatile phenols in the leachate does not exceed 100 mg l^{-1} . Calculations of the distribution of phenols in the subsurface air layer by IMIT program show that even by neutralization of leachate in ponds the maximum concentration of phenols does not exceed $35 \text{ } \mu\text{g m}^{-3}$ under unfavourable weather conditions and decreases to $9 \text{ } \mu\text{g m}^{-3}$ at 1 km, which is 5.5 times less than the maximum permissible limit concentration in the ambient air (LPC = $50 \text{ } \mu\text{g m}^{-3}$ per hour [11]).

Table 12. Maximum Emission Intensity and Annual Emission of Phenol and Methylphenol in the Case of Their Simultaneous Occurrence in Leachate

Parameters	Phenol	3-Methylphenol
Initial data		
pH of wastewater	9.4	9.4
Maximum temperature of water, °C	21	21
Concentration of phenols in water, mg l^{-1}	26.5	17.5
Background concentration in air, $\text{ } \mu\text{g m}^{-3}$	4	1
Results of calculations		
Maximum concentration in air over the ponds, $\text{ } \mu\text{g m}^{-3}$	9.3	1.5
Emission intensity I_f , g s^{-1} :		
$c_f = 0 \text{ } \mu\text{g m}^{-3}$	0.0208	0.0032
$c_f = 5 \text{ } \mu\text{g m}^{-3}$	0.0023	0.0012
Annual emission, tons:		
$c_f = 0 \text{ } \mu\text{g m}^{-3}$	0.221	0.072
$c_f = 5 \text{ } \mu\text{g m}^{-3}$	0.048	0.028

At flowing of leachate *via* the channel system and rivers, the reaction of wastewater changes slowly from alkaline to neutral, and dissolved phenols are partially volatilized or undergo biodegradation. Calculations in [10] prove that in the Purtse River only 15 % of the initial amount of volatile phenols directed into the channel remain. It is difficult to calculate directly the biodegradation efficiency in the channel, the Kohtla River and the Purtse River. For this reason it was supposed that about 50 % of the total amount of volatile phenols would be volatilized and 50 % degraded. Thus, the annual emission of volatile phenols totals *ca* 12 t. Whereas the emission of this quantity of phenols is dispersed over a large territory, the concentration of volatile phenols in the air does not apparently exceed the level of LPC.

Conclusions

The stabilization ponds have a stabilizing effect on physical and chemical parameters of the leachate from oil shale ash dump and prevent considerable fluctuations of pH and pollutant content in effluent. While leachate passes the ponds, its pH value increases from 9.4 to 11.2, which is caused by

building materials of walls and bottom of ponds – i.e. alkaline oil shale ash. Concentration of volatile phenols in the ponds decreases slightly – about by 5 %.

On the grounds of experiments in the laboratory pilot model and theoretical calculations the formulas were elaborated for calculation of emission intensity and annually emitted amounts of phenols into the air depending on leachate temperature and pH, as well as on the phenol concentration in water and their background level in the air.

It was shown that under the following conditions of pond exploitation: pH ~ 11, the concentration of phenols in the leachate *ca* 41 mg l⁻¹, and the minimum background concentration of phenols in the air 5 µg m⁻³, the emission from the surface of ponds remains minimal since phenols are nearly completely dissociated into ions. If the water pH decreases down to 9.4, the maximum emission intensity of phenols (phenol and 3-methylphenol) equals 0.0035 g s⁻¹ and their total annual quantity 0.07 t. While flowing from the ponds *via* the channel, the Kohtla River and the Purtse River, the leachate is neutralized and dissolved phenols partially undergo biodegradation or will be emitted. Thereby their annual emission quantity totals 12 t.

It seems to be clear that the stabilization ponds do not increase the atmospheric air pollution level with phenols essentially. The concentration of phenols in the air close to the ponds varies within the range of 4–50 µg m⁻³ and is caused mainly by their background concentration (by other emission sources).

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REFERENCES

1. Handbook of Atmospheric Air Control (RD 52.04.186–89) / State Committee of Hydrometeorology. – Moscow, 1991. P. 265–267 [in Russian].
2. ISO 6439-84. Water Quality. Determination of Phenol Index by 4-Aminoantipyrine. Spectrometric Methods after Distillation. 1984.
3. *Liblik V., Kundel H., Rätsep A.* The imitation system for assessment of the formation of multicomponential air pollution level // Proceedings of GIS-Baltic

- Sea States '93 Conference. Nov. 29 – Dec. 1, 1993 / H. Vilu and R. Vilu (Eds). Tallinn, 1994. P. 131–138.
4. OND-86. The Method for Calculation of Concentrations of Harmful Substances Contained in the Releases of Enterprises into Atmospheric air. – Leningrad, 1987. P. 3–48 [in Russian].
 5. Kundel H., Aitsen E. Characterization of phenol-containing wastewaters of Oil Shale Processing Association in Kohtla-Järve // Oil Shale Industry. 1986. No. 5. P. 15–17 [in Russian].
 6. Handbook of Chemist. Vol. 5. – Moscow-Leningrad, 1964. P. 276–277 [in Russian].
 7. Dierichs A., Kubička R. Coal Phenols and Bases. – Moscow, 1958. P. 276–277 [in Russian].
 8. Kireev V. Physical Chemistry. – Moscow : High School Publishing House, 1968. P. 264.
 9. Estonian Encyclopaedia. Vol. 2. – Tallinn, 1994. P. 131–138 [in Estonian].
 10. Talpsep E., Heinaru E., Laht T., Heinaru A., Wand H., Stottmeister U. Functional dynamics of microbial populations in water contaminated with phenolic leachate // Oil Shale. 1997. Vol. 14, No. 4. P. 435–453.
 11. Limit Permissible Concentrations for Ambient Air. Regulation No 5, 25.01.1999 of Estonian Ministry of Environment. – Tallinn, 1999.

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