

WASTEWATER TREATMENT IN OIL SHALE CHEMICAL INDUSTRY*

I. KAMENEV**, R. MUNTER, L. PIKKOV

Department of Chemical Engineering,
Tallinn Technical University
5 Ehitajate Rd., 19086 Tallinn, Estonia

L. KEKISHEVA

Oil Shale Research Institute
35 Järveküla Rd., 30328 Kohtla-Järve, Estonia

Process water and phenols' balances for the two processes of oil shale thermal treatment, Kiviter (in vertical retort) and Galoter (with solid heat carrier) were compiled. Options of wastewater treatment in the Kiviter process were analyzed in more detail. Laboratory experiments of biological oxidation of the process water after the dephenolation stage without other effluents and municipal wastewater were carried out. Experiments indicated that the oil shale phenols are generally quite easily degradable when the need for phosphorus is covered by added reagents. The experiments indicated that, compared to conventional aerobic bio-oxidation, the combined process, namely aerobic bio-oxidation with ozonation in re-circulation system, enabled to increase the efficiency of purification at relatively low ozone dosages. Application of ozone at moderate doses (up to 30 mg/L) improved the rate of pollutant removal. Injection of ozone at small dose – 2 mg/L – into the activated sludge in the bioreactor increased the sludge activity: the specific oxygen uptake increased about 15–20%. The biologically treated wastewater can be used as some kind of technological water (cooling water) after chemical precipitation and reduction of sulphate content. It can also be discharged to nature, but only after additional treatment to reduce nitrogen content and after filtration to remove the residual suspended solids.

Introduction

Background

Oil shale is one of the most important natural resources in Estonia. In the year 2002, 12 million tons of oil shale was mined. From this amount about

* Presented at Symposium on Oil Shale in Tallinn, Estonia, November 18–21, 2002.

** Corresponding author: e-mail ikam@edu.ttu.ee

9 million tons were burnt in thermal power plants to produce energy, and about 3 million tons were treated thermally to produce oil.

Thermal processing of Estonian oil shale and refining of the products of its semicoking process (retorting) is accompanied by the formation of large amounts of different process water and wastewaters containing phenols, tar and several other products heavily separable and toxic to the environment. The solid waste of the thermal treatment process, semicoke, is discharged from the retorts and disposed of in an ash dump. Water enters the technological process of oil shale thermal treatment from different sources: physical moisture in mined oil shale; water from oil shale semicoking process (process water); precipitation on the factory's territory; leakages in the cooling water system; used potable water and washwater, etc.

All effluents from oil shale thermal treatment by the *Kiviter* process are concentrated into three main wastewater streams: 1) process water containing mainly physically and chemically bound water liberated during semicoking; 2) industrial wastewater containing effluents of different origin, collected from the factory's territory; 3) ash dump leachates containing different dissolved pollutants (phenols, mineral salts) from semicoke and other deposited solid wastes.

The first stream passes through the complicated treatment process for oil and phenol removal, and is led to the aerobic bio-treatment plant. The second stream passes through the local purification unit, where the coagulation and flotation processes are used for pretreatment. The third stream is collected in several ditches on the foot of the ash dump, one part is taken back for the semicoke extinction, another, less polluted part, is discharged to the Gulf of Finland.

The main treatment stages for the phenolic effluents from the *Kiviter* process are: 1) deoiling (oil separation) [1–3], 2) dephenolation, and 3) biological treatment.

The process waters formed in amount of 150 dm³ per ton of retorted oil shale are directed to the first treatment stage – deoiling. Process waters are deoiled to obtain water-soluble phenols of required quality. These waters are purified from emulsified oils by the method of countercurrent flow extraction in the deoiling column. Gasoline fraction of shale oil, boiling to 180 °C, is used as extractant for emulsified oils [1].

Water with residual oil content of 20–40 mg/L and phenol concentration of 6–11 g/L enters the next purification stage – dephenolation.

Dephenolation process serves two goals: water purification and obtaining marketable products – total water-soluble phenols. It is possible to direct the dephenolated water for additional extraction of water-soluble phenols from the shale oil fraction 230–320 °C, and to redirect it to dephenolation (with oil content of 35–50 mg/L). It would both increase the yield of water-soluble phenols and reduce the amount of water given to the biological treatment.

Dephenolated water is led together with industrial and domestic wastewater to the third stage – biological treatment. The effluent is treated in two

stages at the aerobic bio-oxidation plant, and after purification the water is discharged into the Gulf of Finland. The excess sludge treatment stage is at present lacking, and the sludge is pumped as a suspension of the concentration of about 9 g/L to the ash dump. With this sludge a quite considerable amount of biologically treated water is dispersed as well – about 0.4 m³/ton of treated oil shale.

The *Galoter* process was designed for thermal processing of fine-grain shale (particle size below 25 mm) by the solid-heat-carrier method. The ash, residue of oil shale burning, is used as heat carrier. The design capacity of the retort plant is as high as 1.9 million tons per year. At present 125 tons per hour of raw shale (with a moisture content of 11–12%) is processed.

The *Galoter* process is characterized by the following wastewater flows: 1) wastewater from hydraulic ash removal (HAR), 2) phenolic water, 3) precipitation water from the industrial site.

Water from HAR is run in a closed cycle. The solid material from the ash cyclones and electric filters (ash mixed with fine fraction of dry shale in the mass ratio of 99.8/0.2) is contacted with recycle water in wash-out facilities of the plant, then collected in the sludge tank and directed to mixing with the alkaline aqueous ash suspension from firing oil shale in the power station boilers. The resulting suspension of solid waste material is directed to the settling area of the ash ponds. In the inclined area of the latter the solid portion of the suspension is settled, and the water is recycled to wash-out facilities.

Phenolic water formed in the condensation process of shale oil vapors is directed into the boilers of the power station to fire the phenols. Phenolic water yield in the *Galoter* process is 20–25 kg per ton of dry shale. This water is mainly formed at thermal processing of organic substances of shale, since shale moisture is removed at drying (Table 1).

Table 1. Characterization of Phenolic Water of *Galoter* Process

Items	Content, mg/L
Total phenols	1500–2000
Total sulphur	186.7
Chlorides	3.3
Ammonium nitrogen	486
Nitrate and nitrite nitrogen	147.4
Volatile acids as acetic acid	6720
Volatile bases as ammonium ion	1800
Dry residue	1804
Ignition residue	284

Treatment and Use of the *Kiviter* Process Phenolic Water

During the period of 1991–1998 intensive studies on chemical oxidation of different phenolic effluents (containing phenol, cresols, resorcinols, 5-methylresorcinol, etc.) were carried out at the Chemical Engineering Department of Tallinn Technical University [4–8]. Ozone, hydrogen peroxide, UV-radiation as well as advanced oxidation processes such as O₃/H₂O₂, O₃/UV, H₂O₂/UV, H₂O₂/Fe(II), O₃/H₂O₂/UV were tested. It was shown that,

in principle, the concentration of phenols could be reduced almost by any oxidation method studied. The toxicity of the treated wastewater to *Daphnia magna* decreased with increasing of applied oxidant dose. However, oxidation with molecular ozone and O_3/H_2O_2 had the most potential for practical application. Methods not including ozone (H_2O_2 , UV, H_2O_2/UV , $H_2O_2/Fe(II)$) had, in general, lower efficiency for total phenols' reduction than the methods combining ozone. All the methods tested were quite costly.

If more stringent requirements have to be met, biological treatment can be combined with tertiary treatment such as ozonation or membrane filtration. It has been shown that combined treatment schemes may have a high potential for treatment of recalcitrant wastewaters like the effluents from pulp and paper, chemical, textile, food and dye industry, landfill leachates, etc. During last years, special attention was paid to the recycling combinations of biological treatment and chemical oxidation [9–11].

In this work the main attention has been paid to the questions of treatment and use of only semicoking water without any additional effluents. Formation of this process water cannot be avoided, whilst the presence and amount of other effluents depend on the organization of production on the certain territory as well as on possible co-operation between the companies.

The main aim of purification of the process water and wastewaters is to decrease the content of toxic substances (especially phenols) in wastewater discharged into the natural water reservoirs. Besides, as a result of local treatment, phenols can be obtained – a valuable raw material for the synthesis of many chemical products.

The aim of the present study was also to compare the two oil shale thermal treatment processes, the *Kiviter* and the *Galoter* processes (with solid heat carrier) from the point of view of amount and treatment scheme of phenolic effluents as well as of the yield of water-soluble phenols; to compile the general water flow scheme through the shale oil production in the *Kiviter* process up to the biological treatment plant; to compile the balances of water and pollutants to analyze the efficiency of the biological treatment process for phenols removal and to search for additional chemical oxidation methods to improve the biological process efficiency if needed.

Materials and Experimental Methods

Water Balances

The general water flow scheme of the *Kiviter* process unit was compiled. As the amount of chemically treated oil shale per year varied remarkably, the water and pollutant balances were expressed per 1 ton of technological oil shale. It was impossible to take the actual flow rates for the basis because, due to the joint sewerage, the stream contains pollutants from different productions. To separate the part of oil shale chemical treatment, different computational methods, industrial information and balance calculations have

been used. The amounts of the most important pollutants entrained with water have been indicated.

Experimental Study of Phenolic Wastewater Treatment – Aerobic Bio-Oxidation and Aerobic Bio-Oxidation with Ozonation

Apparatus

The experimental device was used for the experiments with aerobic bio-oxidation and aerobic bio-oxidation combined with ozonation (Fig.1). The device consisted basically of the laboratory bioreactor and the re-circulation system equipped with ozone generator and ozonation column where the re-circulating biologically treated water was treated with ozone. Ozone-air mixture was generated in the corona discharge ozone generator (*Clear Water Tech*, model P-2000) fed by dry air.

Additional facilities were: air compressor, dosing pumps, and analytical apparatus. The laboratory bioreactor was an aerobic activated sludge reactor with the aeration chamber of the volume of 7.5 L and settling chamber of the volume of 2.5 L. The device was operated in the continuous-flow mode and its long-lasting uninterrupted operation (more than a year) was maintained by an automatic control system.

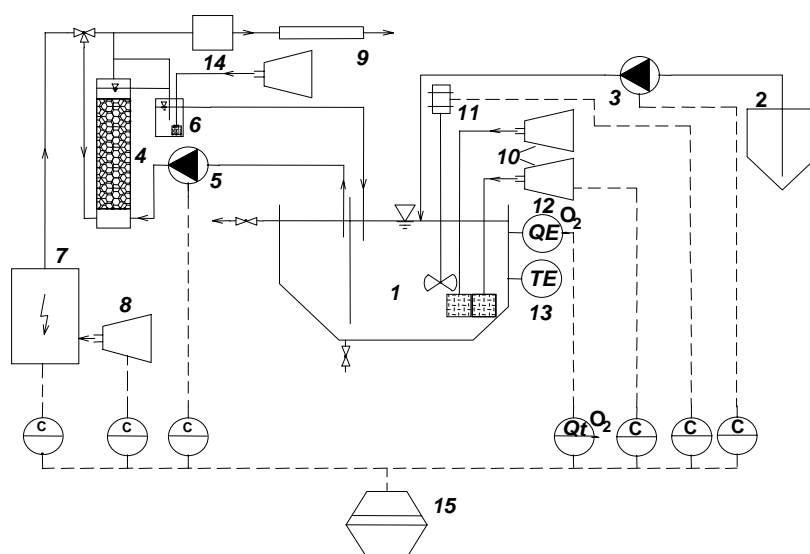


Fig. 1. Activated sludge reactor with the re-circulation system: 1 – aerobic activated sludge reactor, 2 – feed storage container, 3 and 5 – pumps, 4 – ozonation column, 6 – ozone-separation unit, 7 – ozone generator, 8 and 10 – air compressors, 9 – residual ozone-destruction unit, 11 – agitator, 12 – dissolved oxygen concentration sensors, 13 – temperature sensors, 14 – ozone analyzer *Anseros GM-6040*, 15 – controlling PC

In the experiments with aerobic bio-oxidation only the aerobic bioreactor was used. The activated sludge was obtained from Kohtla-Järve Wasterwater Treatment Plant (WWTP). In the combined treatment studies (biological oxidation with ozonation) the re-circulation system was operated.

The experiments of post-ozonation were conducted in a 0.9-L semi-batch glass reactor with continuous gas flow-through. Ozone-air gaseous mixture was generated in the ozone generator OZON-2M.

For the experiments of aerobic bio-oxidation with ozone injection directly into the activated sludge in the bioreactor, the laboratory equipment was rearranged: the ozonation column in the re-circulation system was replaced with a bubble reactor, where the distilled water was saturated with ozone. This water, containing dissolved ozone, was led directly into the activated sludge. The experiments were carried out at the same organic load as in the combined process. The sludge activity was characterized by the oxygen uptake rate.

Phenolic Wastewater

The object of the laboratory studies was the semicoking water of the *Kiviter* process after extraction of phenols with butylacetate (dephenolated process water). The amount of this water comprises approximately 0.14 m³ per 1 ton of the oil shale treated.

Detailed analysis of the content of compounds after extraction at the chemical plant has not been carried out. However, the average annual concentrations of the most important compounds have been determined, mg/L: chemical oxygen demand (COD) 4500, a seven-day biochemical oxygen demand (BOD) 2400, suspended solids (SS) 33, total nitrogen 620, monobasic phenols 11, dibasic phenols 95, sulfates 295, buthylalcohol 230, and buthylacetate 200.

In experiments the phenolic effluent was diluted. The parameters of wastewater changed in a quite wide range: COD ranged from 500 to 3600 mg/L, BOD from 150 to 1100 mg/L and total phenols from 5 to 50 mg/L.

Analyses

The amount of organic matter in the influent and treated wastewater samples was determined as COD, and the amount of biodegradable organic matter – as BOD. The COD and BOD of wastewater were measured by standard methods and concentration of different phenols by a liquid chromatograph. Ozone concentration in the liquid phase was measured using the indigo method proposed by Bader and Hoigné [12], and ozone concentration in the gaseous phase – using ozone analyzer *Anseros* GM-6040. Biomass concentration in the bioreactor and sludge volume index were also determined.

Results and Discussion

Three aspects should be kept in mind considering the treatment and usage of semicoking water of the *Galoter* and *Kiviter* processes: water as a source of valuable products, water as a liquid waste that must meet certain environmental requirements before discharge to the nature, and water as a technological raw material worth saving and recycling in the industrial process.

Comparison of the *Kiviter* and *Galoter* Processes

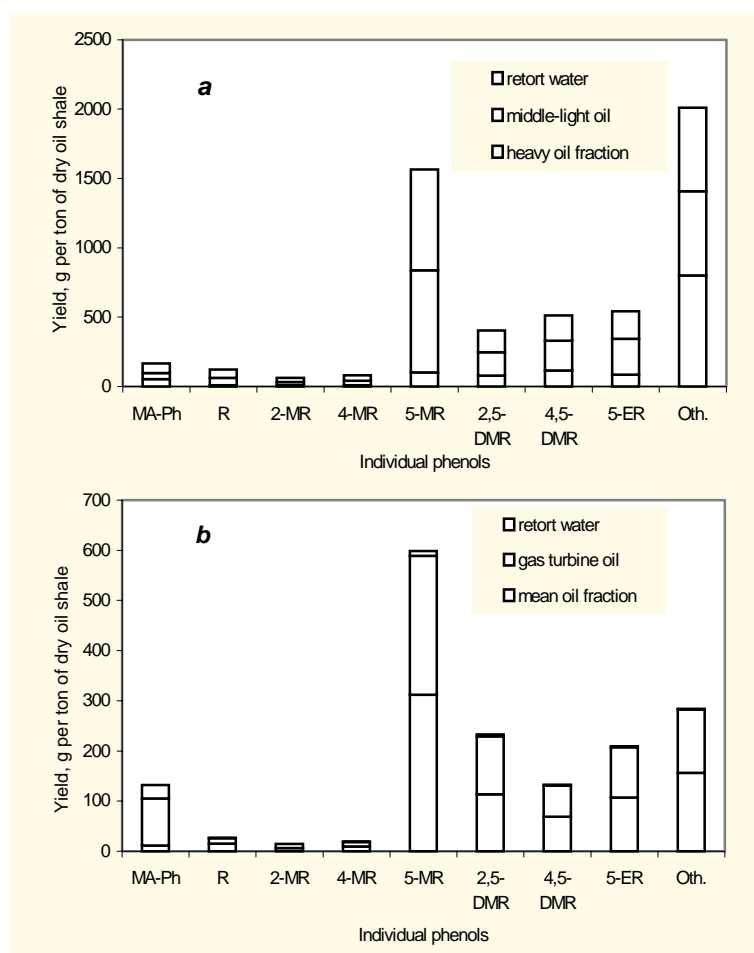


Fig. 2. The yield of individual phenols in *Kiviter* (a) and *Galoter* (b) processes: MA-Ph – monoatomic phenol, R – resorcinol, 2-MR – 2-methylresorcinol, 4-MR – 4-methylresorcinol, 5-MR – 5-methylresorcinol, 2,5-DMR – 2,5-dimethylresorcinol, 4,5-DMR – dimethylresorcinol, 5-ER – 5-ethylresorcinol, Oth. – other resorcinols

The total yield of phenols from the *Kiviter* process is over 5.4 kg per ton of processed oil shale, that of 5-methylresorcinol exceeding 1.5 kg/t. Long-chain, so-called ‘the other alkylresorcinols’ constitute about 35% and monoatomic phenols about 3% of total water-soluble phenols. The distribution of phenols between shale oil fractions and retort water produced by the *Kiviter* process was determined earlier [13–15] and is illustrated here by the diagram in Fig. 2a. The yield and composition of water-soluble phenols present in phenolic water, gas-turbine fuel and mean oil of the *Galoter* process is given by diagram in Fig. 2b.

The total yield of water-soluble phenols from the *Galoter* process is about 1.7 kg per ton of dry shale, i.e. about three times less than that of the *Kiviter* process. Monobasic phenols constitute about 60, 12, and 1.5% of water-soluble phenols present in phenolic water, gas-turbine fuel, and mean oil, respectively. Alkylresorcinols constitute about 36, 70, and 75%, respectively.

The composition of the recycle water from the hydraulic ash-removal system was investigated. In compliance with European Council Directive (Council Directive – 1999/31/EC), the level of hazard of solid wastes in aqueous eluates was evaluated (DIN 38414-84). Comparison of the results of recycle water analyses with the standards indicated that the pH is insignificantly higher (13.2 instead of the maximum permitted limit 13.0). However, the content of sulphates in the recycle water is approximately 3 g/L (permitted limit is 1 g/L). This may be probably explained by repeated (multiple) eluation of the ash produced by the *Galoter* process as well as of the ash from oil shale burning at the power plant.

Going on with the data collection and product analysis of the *Galoter* process, the flowsheet of this process was composed, and the amounts of the main intermediates and final products were determined per 1 ton of dry initial oil shale. The results of the calculations on amounts of water and phenols are presented in Table 2. For comparison, the corresponding data on the *Kiviter* process are presented as well.

Table 2. Comparison of the *Kiviter* and *Galoter* Processes

Product, kg per 1 ton of oil shale	<i>Kiviter</i>	<i>Galoter</i>
Total amount of oil	160	148
Phenols in oil	26.7	24
Water of semicoking	140	23
Pollutants in water of semicoking after dephenolation:		
BOD	0.346	0.345*
Total amount of phenols	0.18–0.34	0.046
Phenols	0.0146	0.046*
Volatile phenols	0.0016	0.025*
Total nitrogen	0.087	0.014

* Nowadays, in the *Galoter* process phenols are not separated from the semicoking water; they are burnt together with other compounds.

Wastewater Treatment in the Kiviter Process

Table 3 summarizes the amounts of pollutants in kg per 1 ton of treated oil shale at the inlet and outlet of the biotreatment plant taking into account the leachate from the ash dump as well.

Table 3. Balance of Pollutants of the Kiviter Process

Indices	Wastewater to biotreatment	Ash dump leachate to biotreatment	From biotreatment to the environment	From ash dump to the environment	Total with wastewater to the environment
Water or leachate, m ³ /ton	0.47	0.18	0.65	0.34	0.99
BOD, kgO ₂ /ton	0.60	0.033	0.057	0.0127	0.0697
Pollutant, kg per 1 ton of treated oil shale:					
Suspended solids	0.067	0.028	0.066	0.011	0.077
Oil products	0.004	–	0.0008	–	0.0008
Total nitrogen N	0.096	0.0007	0.029	0.00053	0.0295
Monobasic phenols	0.021	0.0055	0.00047	0.0032	0.00367
Dibasic phenols	0.039	0.0046	0.0065	0.00013	0.00663
SO ₄ ²⁻	0.47	0.047	0.46	0.0186	0.478

Discharge of the Treated Wastewater to Nature

At the present time there are no maximum permissible concentrations (MPC) for phenols in natural water reservoirs. The concentration of monobasic and dibasic phenols at the outlet of the aeration tanks in 2000–2002 has met or been very close to the established Estonian MPC standards for the biologically treated effluent discharged to the Gulf of Finland – 0.1 mg/L for volatile phenols and 15 mg/L for total phenols (Table 4).

Table 4. Typical Results of Wastewater Analysis Prior to and After Bio-Treatment at the Kohtla-Järve WWTP, and Requirements to the Treated Industrial Effluents in Estonia

Items	Prior to treatment	After treatment	Limiting concentration
BOD, mgO ₂ /L	376	11	15
COD, mgO ₂ /L	951	121	250
Monobasic phenols, mg/L	3.96	0.03	0.1
Dibasic phenols, mg/L	18.0	1.2	15
Total nitrogen, mg/L	49.7	21.6	10
Total phosphorus, mg/L	3.2	1.0	1.5
Sulphates, mg/L	180	172	–
Sulphides, mg/L	2.6	0.2	–
Chlorides, mg/L	277	232	–
Oil products, mg/L	2.2	0.5	1.0
Suspended solids, mg/L	119	27	15

It is important to keep in mind here that these results have been obtained in the conditions of joint biological treatment of all phenolic effluents including the sewage from local settlements. The most important question now is – how high purification degree can be obtained when the *Kiviter* process water after the dephenolation stage is treated alone without addition of other effluents and sewage.

Table 5. Efficiency of the Biological Oxidation Process in the Laboratory Bioreactor

Parameter	Before biological treatment	After biological treatment
BOD, mgO ₂ /L	2400	6–7
COD, mgO ₂ /L	4500	240–300
Suspended solids, mg/L	33	15–20
Total nitrogen, mg/L	620	500–550
Monobasic phenols, mg/L	11	0.13–0.17
Dibasic phenols, mg/L	95	0.5–1.0
Suspended solids, mg/L	295	290–300

Our laboratory studies on biological treatment, as well as the biodegradability tests with pure phenols have proved that the oil shale phenols are generally quite easily degradable when the need for phosphorus is covered by added reagents (Table 5).

If to compare the quality parameters of the treated phenolic effluent with the requirements established in Estonia **for the effluents dis-**

charged to the nature, one can conclude that the treated phenolic effluent meets the guidelines for BOD, COD, one-basic and two-basic phenols, but does not meet the guidelines for SS and nitrogen content (see Table 4). The problem with suspended solids can be relatively easily solved by introduction of a complementary filtration stage, but reduction of the nitrogen content needs introduction **of a new, anaerobic treatment stage**, of course, with the corresponding investment costs.

The biologically treated effluent does not meet the requirements for the natural water mainly due to the residual values of the COD, total nitrogen content and color.

Reuse of the Purified Water

According to the Estonian Standard **of the surface water quality classes**, the treated phenolic effluent belongs to the class “satisfactory” by its BOD value, and to the quality class “very bad” by the other parameters [16]. This water can be used only as some kind of technological water in the case of fresh water shortage. It can probably be used as cooling water, but only after additional chemical precipitation and reduction of sulphate content.

Results of the Experimental Study on Aerobic Bio-Oxidation with Ozonation

To maintain hydrodynamic conditions of the system operation, the experiments were carried out as a test series. The tests series was started with the conventional aerobic bio-oxidation process at the retention time of 1.2 day.

The results indicated the efficiency of the purification of 60% for COD reduction and 93% for BOD, the removal of phenolic compounds achieved 85%. Practically all the biodegradable part of organics was removed.

The post-ozonation of biologically treated phenolic wastewater was carried out in a semi-batch ozonation column. The efficiency of the process was relatively low: the ozone dose consumed for COD reduction was 3 to 8 mgO₃ per mgCOD removed. BOD did not change during ozonation, which made the biodegradability of the wastewater, expressed as the BOD/COD ratio, slightly improved by ozonation. The improved biodegradability of wastewater made subsequent aerobic bio-oxidation reasonable, and the combination of bio-oxidation with ozonation in a recycling mode likely to be effective.

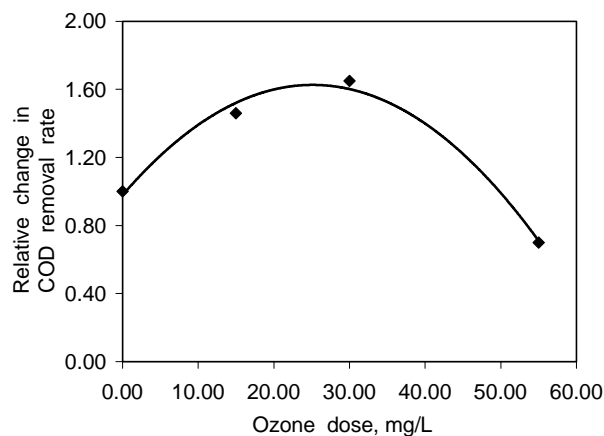


Fig. 3. Change in COD relative removal rate versus applied ozone dose

Next, the combined process, namely aerobic bio-oxidation with ozonation in the re-circulation system, was studied. First of all the process flow sheet was expanded with a re-circulation system, and ozone was injected into the ozonation column. Ozone was applied during the 5–10-day periods (15–55 mg per L of treated wastewater). The changes in the COD and BOD values, and in individual phenol concentration were followed. The rate of the corresponding pollutant removal was calculated (Fig. 3).

The main conclusions were the following. Injection of ozone at moderate doses (up to 30 mg/L) improves the rate of pollutant removal by 50–60%. The increase in the removal rate during the ozone injection period and some decrease between these periods were typical. The achieved improvement in the biological oxidation of phenols by ozone justifies further studies on this combined treatment method for other phenolic effluents (industrial wastewater from the factory's territory, ash dump leachate).

In general, in the combined process, the COD reduction efficiency increased up to 75% and that of BOD decreased for 96%. The optimum ozone dose for maximum COD reduction in the combined process was 60 mg/L at the organic load 2000 mgCOD L⁻¹ day⁻¹.

The comparison of the results obtained from the experiments of conventional bio-oxidation, post-ozonation and combined treatment indicated that the impact of ozone on aerobic bio-oxidation in the combined process concerned not only the increased biodegradability but the residual ozone influenced also the properties of the activated sludge.

Subsequent research was carried out to ascertain the influence of ozone on the biomass activity. The experiments of aerobic bio-oxidation of phenolic wastewater with direct introducing of ozone into the activated sludge in the bioreactor were conducted.

Table 6. Oxygen Uptake Rate Constants in Different Conditions

Process parameters	System	
	Aerobic bio-oxidation	Aerobic bio-oxidation + ozone introduction into activated sludge reactor (ozone dose 2 mg/L)
COD of wastewater in the activated sludge reactor, mgO ₂ /L	290–356	277–304
Biomass concentration, g/L	2.31–2.94	1.42–1.95
Rate constant, mgO ₂ s ⁻¹ gbiomass ⁻¹ (mgO ₂ /L) ⁻¹	0.0012–0.002	0.0016–0.0022

The biomass activity was characterized by the oxygen uptake rate. The experiments were carried out at the same organic load as in the combined process. The results indicated that ozone applied straight to activated sludge in small doses (2 mg/L) did not harm the biomass, but increased the specific oxygen uptake by about 15–20% (Table 6). However, at an ozone dose as high as 4 mg/L, the values of the rate constant were at the same level as in conventional aerobic bio-oxidation. It could be concluded that direct ozonation of biomass affects microbial organisms, improves the composition of biomass (reducing filaments), and appears to be successful at lower ozone doses.

Summarizing, the combination of biological oxidation with ozonation is a prospective method to treat phenolic effluent and in certain limits enables to improve the efficiency of purification and to stabilize activated sludge. However, the mechanism of ozone impact on the biological oxidation process needs further, more detailed studies.

Conclusions

1. The total yield of phenols from the *Kiviter* process is over 5.4 kg per ton of processed oil shale, that of 5-methylresorcinol exceeding 1.5 kg/t. Long-chain, so-called 'the other alkylresorcinols' constitute about 35% and monoatomic phenols about 3% of total water-soluble phenols.

2. The total yield of water-soluble phenols from the *Galoter* process is about 1.7 kg per ton of dry shale, i.e. about three times less than that of the *Kiviter* process. Monobasic phenols constitute about 60, 12, and 1.5% of the water-soluble phenols present in phenolic water, gas-turbine fuel, and mean oil, respectively. Alkylresorcinols constitute about 36, 70, and 75%, respectively.
3. From the point of view of phenols as a valuable product, their separation from the semicoking water of the *Galoter* process is of negligible importance, and treatment of this water with the purpose to separate the phenols is not justified. The *Galoter* process yields only 20–25 kg phenolic water per ton of dry shale. The *Galoter* process produces about six times less efficient than the *Kiviter* process, and the problem of their treatment is in practice solved by the burning in the power station.
4. On the other hand, in the *Kiviter* process approximately 1/3 from all of the most valuable phenols are liberated with the process water, and they are separated during the extraction or dephenolation stage. Untreated phenolic effluents are heavily polluted and cannot be discharged to the nature without purification.
5. During several decades the prevailing point of view has been that the biological treatment process is very sensitive towards the phenol content, and that is why the addition of other effluents, especially sewage, has been considered absolutely necessary.
6. The laboratory studies of biological treatment as well as the biodegradability tests with pure phenols have proved that the oil shale phenols are generally quite easily degradable when the need for phosphorus is covered by added reagents. Biological oxidation of the wastewater from the dephenolation stage of the *Kiviter* process as a single effluent was successfully carried out.
7. The biologically treated wastewater did not meet the requirements for the natural water mainly due to the residual values of the COD, total nitrogen content and color. This water can be used only as some kind of technological water in the case of fresh water shortage. It probably can be used as cooling water, but only after additional chemical precipitation and reduction of sulphate content.
8. Comparing the quality parameters of the biologically treated phenolic wastewater with the requirements established in Estonia for the effluents discharged to the nature, one can conclude that the treated phenolic effluent meets the guidelines for BOD, COD, one-basic and two-basic phenols, but does not meet the guidelines for suspended solids and nitrogen content. The problem with suspended solids can be relatively easily solved by introduction of the complementary filtration stage, but reduction of the nitrogen content needs introduction of a new, anaerobic treatment stage with the corresponding investment costs.

9. In the combined process – aerobic bio-oxidation with ozonation in the re-circulation system – the COD reduction efficiency increased up to 75%, and BOD decreased for 96%. The optimum ozone dose for the maximum COD reduction in the combined process was 60 mg/L at the organic load 2000 mg COD/(L day). Thus, the combined process is a prospective method for purification of phenolic wastewaters.
10. Comparison of the experimental results indicated that the impact of ozone on the aerobic bio-oxidation in the combined process did not concern only increased biodegradability, but the residual ozone influenced positively also the properties of the activated sludge. The activated sludge was not deteriorated, and the specific oxygen uptake increased for about 15–20% as a result of the small ozone dose – 2 mg/L – introduced straight to the biomass.

Acknowledgements

This study was supported by the USA–Estonian Oil Shale Programme, the Estonian Scientific Foundation (Grant No. 4263) and Maj and Tor Nessling Foundation (Finland).

We also thank Dr. Marina Trapido for the chromatographic analyses of phenols.

REFERENCES

1. *Vetik, Yu.R., Artamonova, V.V.* Experience with petrol fraction application for phenols removal from phenolic process water // *Oil Shale : Information Series I / EstNIINTI (Estonian Institute for Scientific and Technical Information)*. 1979. No. 6. P. 26–27 [in Russian].
2. *Volkov, L., Shmidt, L.* Dephenolation of phenolic and industrial effluents by pressure flotation // *Ibid.* 1962. No. 4. P. 34–39 [in Russian].
3. *Tcurikova, U.P., Ratsep, A.J.* Water bodies protection from the effluents from oil shale chemical industry // *Oil Shale Industry : Information Series I*. 1985. No. 5. P. 21–22 [in Russian].
4. *Kallas, J., Pikkov, L., Viiroja, A., Kamenev, S., Joarand, H., Tali, E., Munter, R., Palosaari, S.* Treatment technology of wastewater containing phenols and phenolic compounds // *Lappeenranta, Finland : LUT Research Paper No. 26*. 1992.
5. *Trapido, M., Veressinina, Y., Munter, R.* The application of ozonation and advanced oxidation processes for degradation and detoxification of phenolic compounds // *Proc. 14th Ozone World Congress, Dearborn, MI, USA*. 1999. Vol. 1. P. 235–249.
6. *Trapido, M., Munter R., Veressinina, Y.* Advanced oxidation processes as an opportunity for purification of wastewater from Estonian oil-shale industry // *J. Env. Eng.* 1998. Vol. 124, No. 8. P. 519–534.

7. Kamenev, S., Kallas, J., Munter, R., Trapido, M. Chemical oxidation of biologically treated phenolic effluents // *Waste Management (USA)*. 1995. Vol. 15, No. 3. P. 203–208.
8. Preis, S., Kamenev, S., Kallas, J., Munter, R. Advanced oxidation processes against phenolic compounds in wastewater treatment // *Ozone : Sci. and Eng.* 1995. Vol. 17, No. 4. P. 399–419.
9. Ried, A., Mielcke, J. The state of development and operational experience gained with processing leachate with a combination of ozone and biological treatment // *Proc. 14th Ozone World Congr., Dearborn MI, USA*. 1999. Vol. 2. P. 65–81.
10. Ledakowicz, S., Solecka, M. Influence of ozone and advanced oxidation processes on biological treatment of industrial wastewater // *Proc. Int. Conf. Appl. Ozone*. Berlin, 2000. P. IV5.1–16.
11. Jeworski, M., Heinzle, E. Combined chemical-biological treatment of wastewater containing refractory pollutants // *Biotech. Ann. Rev.* 2000. No. 6. P. 163–196.
12. Bader, H., Hoigne, J. Determination of ozone in water by the indigo method: a submitted standard method // *Ozone : Sci. and Eng.* 1982. No. 4. P. 169–176.
13. Tüikma, L., Molder, L., Tamvelius, H. Resources of water-soluble alkylresorcinols in oil fractions and retort water formed by processing oil shale in generators of high unit capacity // *Oil Shale*. 1991. Vol. 8, No. 4. P. 350–354.
14. Kundel, H.F. Determination of alkylresorcinols content in phenolic effluents // *Oil Shale : Information Series I / EstNIINTI (Estonian Institute for Scientific and Technical Information)*. 1979. No. 6. P. 17–20 [in Russian].
15. Kundel, H.F., Aitsen, E.E.-V. Gas-chromatographic analysis of strait distillation fractions of water-soluble phenols // *Ibid.* 1981. No. 10. P. 24–27 [in Russian].
16. Regulation of the Minister of Environment No. 33 22.06.2001. Surface Water Bodies, Quality Classes and Reference Methods.