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SHORT REVIEW OF INVESTIGATIONS ON THE TREATMENT OF OIL SHALE INDUSTRY WASTEWATERS IN 1960-1990

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This paper summarizes the results of research on the purification of oil shale industry wastewaters ordered by the then Oil Shale Processing Association in Kohtla-Järve and carried out by several research institutes during thirty years.

The review has been drawn up on the basis of reports by RAS Kiviter, altogether over 40 different papers. The papers were ordered by the Oil Shale Processing Association (Põlevkivikeemia Tootmiskoondis), the predecessor of RAS Kiviter (1964-1990). Some additional information can be probably found from the archives of several research institutions.

The beginning of the period under observation can be associated with an intensive development of oil shale chemical industry. Unfortunately, no adequate measures of nature protection were taken at that time. In [1] a certain depiction of the situation is presented. Amounts of wastewater directed into bodies of water were shockingly big. For instance, the amount of wastewater discharged into the Purtse River monthly exceeded today's yearly amount. At the same time even the so-called conventionally clean waters contained 20-30 mg/l of oil and 30-40 mg/l of total phenols. The Kohtla River was characterized by containing 15 mg/l of phenols and an oil layer at the bottom of the river with the maximum thickness of 0.5 m at places. At the beaches of Aa and Ontika the sea contained phenols 0.2 mg/l. The fish caught here had the smell and taste of phenols.

The disastrous situation demanded a search for solutions and that is the reason why the enterprises of oil shale industry of that time allocated considerable sums of money the related research. A considerable number of research institutions were involved. In addition to the specialists of oil shale industry the following institutions participated:

- Oil Shale Research Institute;
- Tallinn Polytechnical Institute;
- Institute of Chemistry of the Academy of Sciences;
- Leningrad Civil Engineering Institute;
- Hydrochemical Institute affiliated to the Institute of Biology and Inland Waters of the Academy of Sciences of the USSR in Novocherkassk;
- All-Union Hydrological Research Institute;
- Voronezh Department of the Production Trust of Oil Processing Chemical Plants.

The first report dates back to 1964 [2]. The compilers of the report are specialists of the factory of oil shale chemical processing. Operation of the oil removal device (made in 1963) was analysed and a number of proposals were made to improve the unsatisfactory work of the device.

If the reports under examination were classified by the themes dealt with, the first group would include the ones comprising balances of oil shale industry wastewaters and the data on their composition. Oil Shale Research Institute was engaged in this field most thoroughly and the investigations carried out by the institute covered all three factories of oil shale chemistry of that time [1, 3, 4, 5, 12]. Balances are also found in other research works [6, 7, 8]. Oil Shale Research Institute tried to prognosticate the amounts of wastewater of oil shale industry until the year 2000 [9] and even until the year 2010 [10]. Nowadays, due to an abrupt change of the political and economic situation, those prognoses are of historical interest only. Apart from wastewater, the Oil Shale Research Institute also worked on the possibilities of reducing the use of fresh water. Mass consumption of lake water caused the extensive use of air coolers which eventually considerably decreased the consumption of cooling water in oil shale industry. In addition, the possibilities of using phenolic waters to improve the quality of cooling water and to decrease the corrosion were examined [11, 12].

Investigations devoted to the improvement of the work of particular devices make up the second group of reports. These involve a dephenolization device, an oil removal device [2] and wastewater treatment facilities. Oil Shale Research Institute thoroughly examined the dephenolization device [13, 14] and made numerous improvement proposals.

The work of the treatment plant was shortly discussed in earlier research works [4, 5], but a more serious analysis started in the early 1980s, after starting up a new plant. Reports by the Voronezh Department of the Trust of Oil Chemical Processing Plants [15, 16, 17] are of interest. The legal document authorizing the launching of the 1st stage of the new plant pointed out a whole list of faults of the project

and installation. The correction of a number of defects required the reconstruction of separate parts. Unsatisfactory work of the treatment plant coerced specialists into seeking new solutions and already in 1989 Tallinn Technical University and Oil Shale Research Institute worked out projecting regulations for the reconstruction of the plant. [18].

Studies devoted to finding new methods of treatment of phenolic waters form a separate group. Various different methods were tested.

In 1968 the Leningrad Institute of Civil Engineering started its research [19]. The literature list of the reports included 94 works which refers to a thorough preparation. A whole list of different possibilities of the treatment of phenolic waters was examined, but a large part of the work was dedicated to the use of stabilization ponds. It was supposed that after staying in the ponds for 30 days, the amount of volatile phenols would decrease up to 99 % in summer with the process being most intensive during the initial 7-8 days. Reduction of non-volatile phenols was expected to be over 75 %. Laboratory and semi-industrial experiments carried out in 1969 [20] considerably diminished earlier optimism. Although microorganisms that decompose phenols were found, and a conducive role of aeration in the decomposing process of phenols was ascertained, it appeared that an increase of the concentration of volatile phenols over 12 mg/l and the concentration of non-volatile phenols over 200 mg/l led to the formation of anaerobic conditions and brought about an abrupt decrease of the treatment effect.

During the 1970s the Institute of Chemistry dealt with the method of electrical impulse [21, 22]. Later Oil Shale Research Institute continued the investigation of this and other electrical methods [23, 24, 25, 26, 27]. Although the electrical methods made it possible to achieve a comparatively good purification level, they turned out to be too expensive due to a great need for electrical energy.

Experiments carried out in Oil Shale Research Institute on the biochemical oxidation of phenolic waters in a plate-type column [24] are of interest. It was found that on sieve plates the processes proceeded 10-15 times faster than in the aeration basin.

Oil Shale Research Institute also investigated the utilization possibilities of solid sorbents (ionites, activated carbon, coked peat etc.) in wastewater treatment [23], failing, however, to find a satisfactory sorbent.

The report of Oil Shale Research Institute on the experiments of the treatment of phenolic waters in the process of reverse osmosis dates from 1977 [28]. Treatment turned out to be possible, but, however, there was no adequate technical basis in the Soviet Union at that time.

An investigation by the Institute of the Hydrological Geology on the possibilities of wastewater treatment with algae [29] appears to be somewhat exotic. On the basis of experience a conclusion was reached

that it was possible to oxidize phenols completely with the so-called symbiotic activated sludge.

Recently Tallinn Technical University has been investigating the opportunities of the treatment of phenolic waters [30]. The research has been carried on in co-operation with Lappeenranta Technical University [31]. The latest research presents a thorough review of the methods of treating wastewaters with a special attention on ozonation and the use of hydrogen peroxide.

Investigations carried out by the Institute of Hydrochemistry of Novocherkassk in the early 1970s [32, 33, 34] appeared remarkable. Situation of the rivers Kohtla, Erra and Purtse and of the sea at the mouth of the Purtse River was monitored during a number of years. The role of microorganisms in the destruction process of phenols and shale oil was also studied. Several expeditions to the rivers and also to the sea were carried out and a great number of water samples were taken, among them samples from the sea within the radius of 10 km from the mouth of the Purtse River. Attempts were made at the mathematical description and a prognosis of the speed of the degradation of pollutants in the above-mentioned rivers. In laboratory experiments it was determined that if the ratio between shale oil and water is 1 : 10, shale oil has no toxic influence on the microflora of water

Outdoor investigations thoroughly fixed the disconsolate situation of the rivers and the sea. 25 years have passed since that time. Amounts of pollutants discharged into the rivers have decreased essentially. Therefore, repetition of similar investigations would be of great interest.

The subject of reuse of wastewater has also been discussed. Oil Shale Research Institute was the first to investigate the corresponding ways [25]. Later on the Institute of Hydrological Geology having thoroughly dealt with the problem, prepared respective projecting regulations [35] that were specified henceforth [7]. The same Institute worked out the first principal solution of the chemical treatment of ash heaps leachate [36] and its practical implementation started, but the work was discontinued due to the change of the political and economic situation. The Institute of Hydrological Geology carried on the research on ash heaps leachate and in 1991 a report [37] dealing with the methods of biological treatment of those waters was completed. The tests indicated that it was possible to treat the ash heaps leachate biologically.

As it appears from the present review, during the years 1960-1990 an extensive work was done to find suitable possibilities for the treatment of oil shale industry wastewaters. The practical implication of those investigations is that they may avoid useless repetition of the work already done.

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