# Ecological Aspects of Oil Shale Processing

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## Abstract

Oil shale belongs to lean and environmentally challenging fossil fuels, however, it is a mineral with high potential. Leanness of oil shale is determined by its low organic matter content (10-40%), which yields considerable amount of wastes when utilized. On the other hand, the potential of oil shale lies in the fact that the explored oil shale resources, when converted into synthetic fuel produced in thermal processing, exceed explored petroleum reserves by several times. In this case, the ecological aspects of thermal processing are imperative and should be based on the following principles, developed according to the vast experience of oil shale processing in Estonia:

I Oil shale is to be processed in an integrated way with its organic and mineral components utilized at maximum efficiency.

II Technology of oil shale processing is to be flexible in respect to quality of processed raw material.

III Oil shale processing wastes must not cause either short-term or long-term environmental pollution.

IV Consumption of natural resources (water, air, soil) used by oil shale processing is to be minimized.

The ecological risks of oil shale based synthetic petroleum production can be greatly reduced when a comprehensive approach to technology selection is used. The report contains distinctive environmental features of various oil shale processing technologies.

Oil shale belongs to lean and prospective fossil fuels. Leanness of oil shale is determined by its low concentration of the organic matter (10-40%), its prospectiveness, on the other hand, is determined by the fact that the explored oil shale resources expressed in tons of fuel which may be produced by their thermal processing, several times exceed the explored petroleum reserves, and besides, the "availability" of oil shale, i.e. its mining costs (in view of its bedding conditions) are in an average appreciably lower than the mining costs of coal. These considerations and also the expected depletion of the world petroleum reserves in the foreseeable future, inevitably makes oil shale a very prospective fossil fuel.

It is especially important to date, when according to estimations made by the Center of International Strategic Investigations, the global petroleum crisis may be expected in about 40 years, to pay special attention to the ecological aspects of oil shale processing which cannot be considered as fully studied so far.

In spite of numerous studies dealing with environment protection in oil shale mining, energy production based on oil shale and its thermal processing, so far there is no systematic vision on complex environmental problems in this connection.

An ecologically acceptable conception of oil shale thermal processing developed at present by the Institute of oil shale Research at Tallinn Technical University includes the following basic principles:

*I Oil shale is to be processed in a complex way, i.e. its organic and mineral portions should be both most efficiently used.*

*II The technology of oil shale processing has to be sufficiently flexible in respect to quality of feed (in many deposits oil shale has considerably different chemical compositions of its organic and mineral portions and its calorific values even within the same deposit).*

*III Oil shale processing wastes must not cause either short-term or prolonged pollution of environment.*

*IV Consumption of natural resources (water, air, soil) used by oil shale processing is to be minimized.*

This conception, by the vision of its developers, has the hierarchy of priorities shown in Figure 1.

The above hierarchy is based on the priority of development of the basic technologies over fighting the results of inadequately motivated technological decisions.

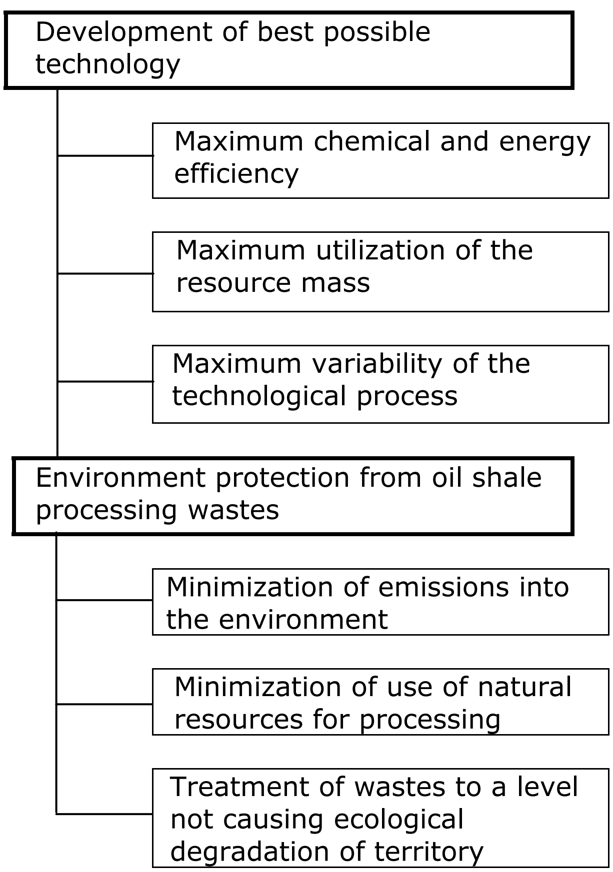


Figure 1: Ecological Priorities in Oil Shale Processing

An historical list of basic technologies for processing oil shale of Baltic deposit, and also technologies developed at different times in Germany, U.S.A., Canada and other countries is given in Fig. 2-6.

1. Vertical retort has no zone for semicoke gasification.
2. Vertical retort with a zone for semicoke gasification.
3. Chamber oven (similar to coke batteries).
4. Lurgi-Ruhrgas process, Chevron STB process.
5. The Galoter process with solid heat carrier.

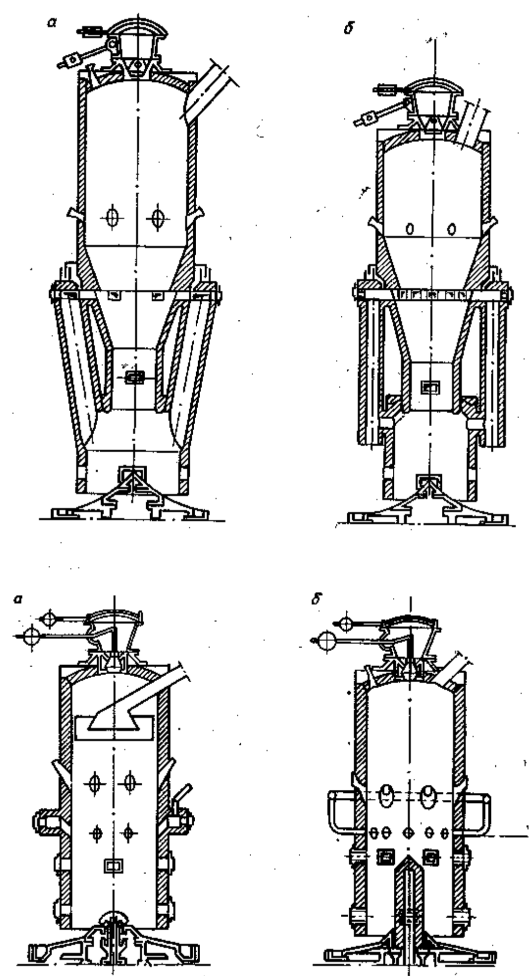

Figure 2: Cross section of vertical retort (no gasification of semicoke).

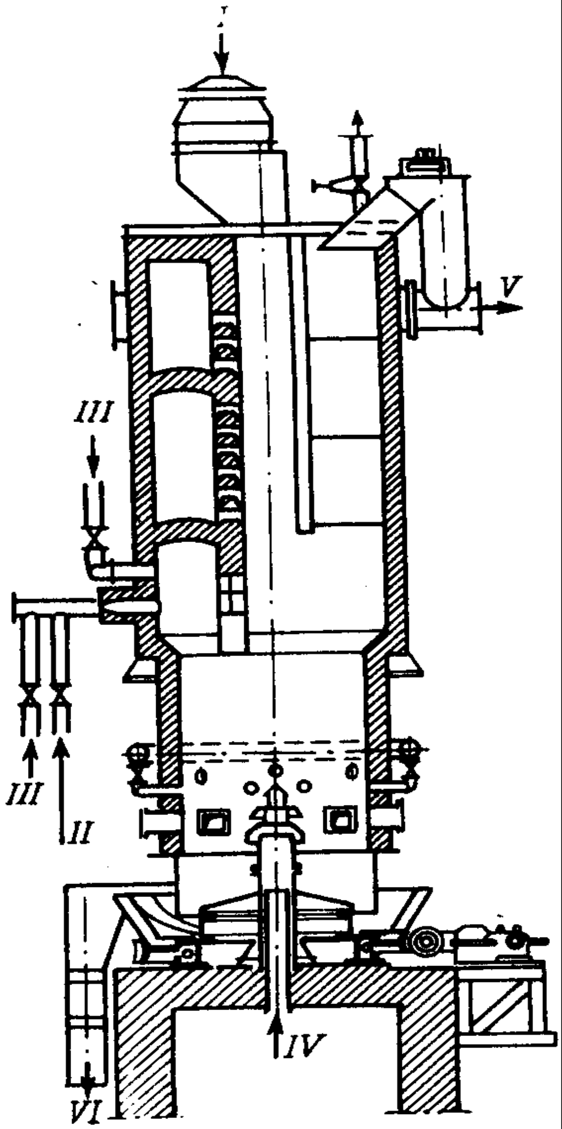


Figure 3: Cross section of vertical retort with zone for semicoke gasification

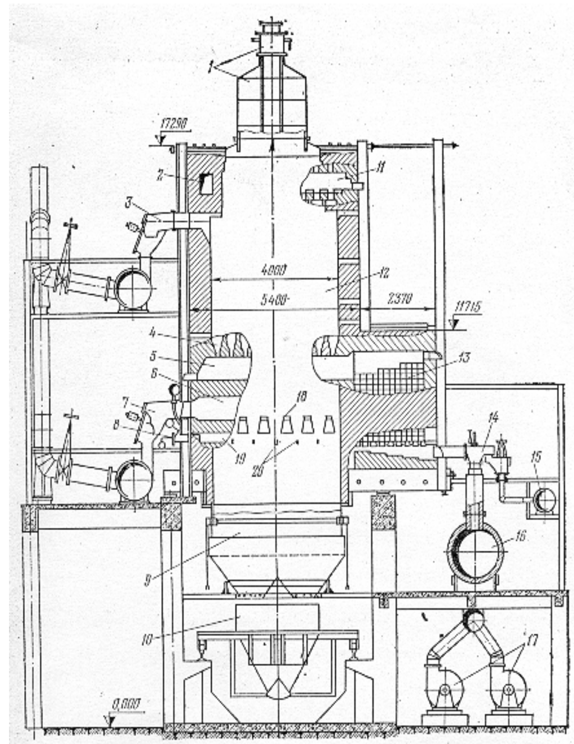

Figure 4: Cross section of the chamber oven

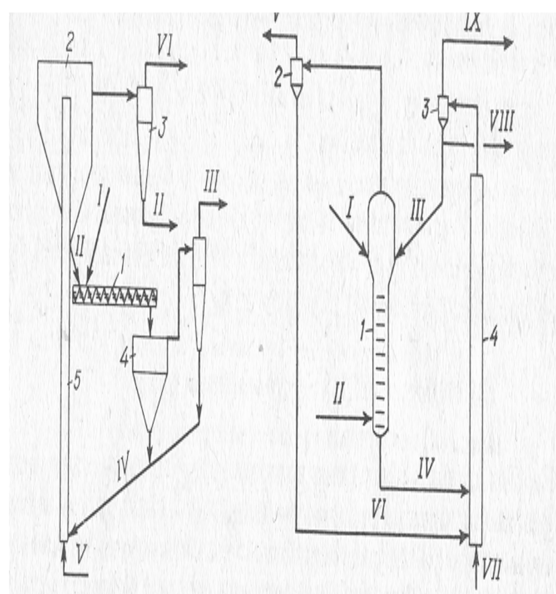


Figure 5: Flow diagrams of the Lurgi-Ruhrgas and Chevron STB processes

From the point of view of ecology the above technologies may be divided into four groups according to heat carrier used, completeness of semicoke processing and the degree of thermal processing of the initial oil shale. To the first group belong the retorts having no gasification of semicoke, to the second group the retorts with gasification or afterburning of semicoke, to the third – processes with deep thermal processing of oil shale, and to the fourth – technologies with shale-derived

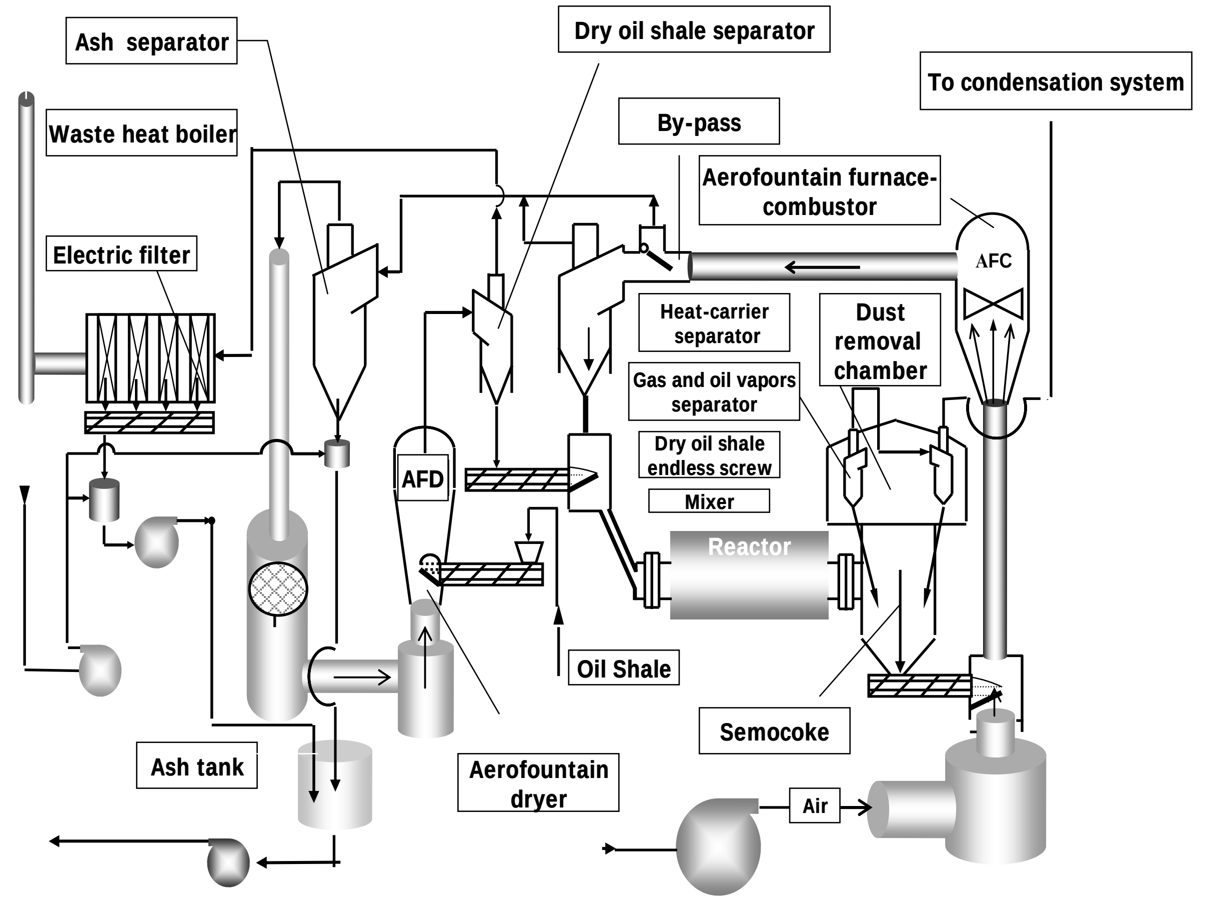


Figure 6: The "Galoter" process flow diagram

ash heat carrier and afterburning of the carbon of semicoke.

From the technological point of view the above four groups of processes are substantially different. Nevertheless, for these processes Table 1 gives the common formulations of ecological requirements.

Unfortunately, to date there are no adequate data at our disposal to make a systematic analysis of all the said technologies according to the above criteria, a qualitative appraisal according to some of the general chemical data is still possible. The following qualitative diagram (Fig. 7) presents an integrated ecological appraisal of oil shale processing technologies according to concentrations of oil, carbon, salts in aqueous leaching of the solid wastes. Darkness of shade in the diagram shows increased concentration of the component. It may be seen in the

**Table 1: Ecological assessment criteria for oil shale processing technologies**

1. *The quantity of wastes produced by the process (solid, liquid, gaseous).*
2. *Concentration and hazard class of the harmful substances contained in wastes produced.*
3. *Ecological mobility of elements contained in wastes.*
4. *Availability of practical methods of environment protection from harmful substances contained in wastes.*
5. *Consumption of natural resources (water, air, soil) for processing technologies.*

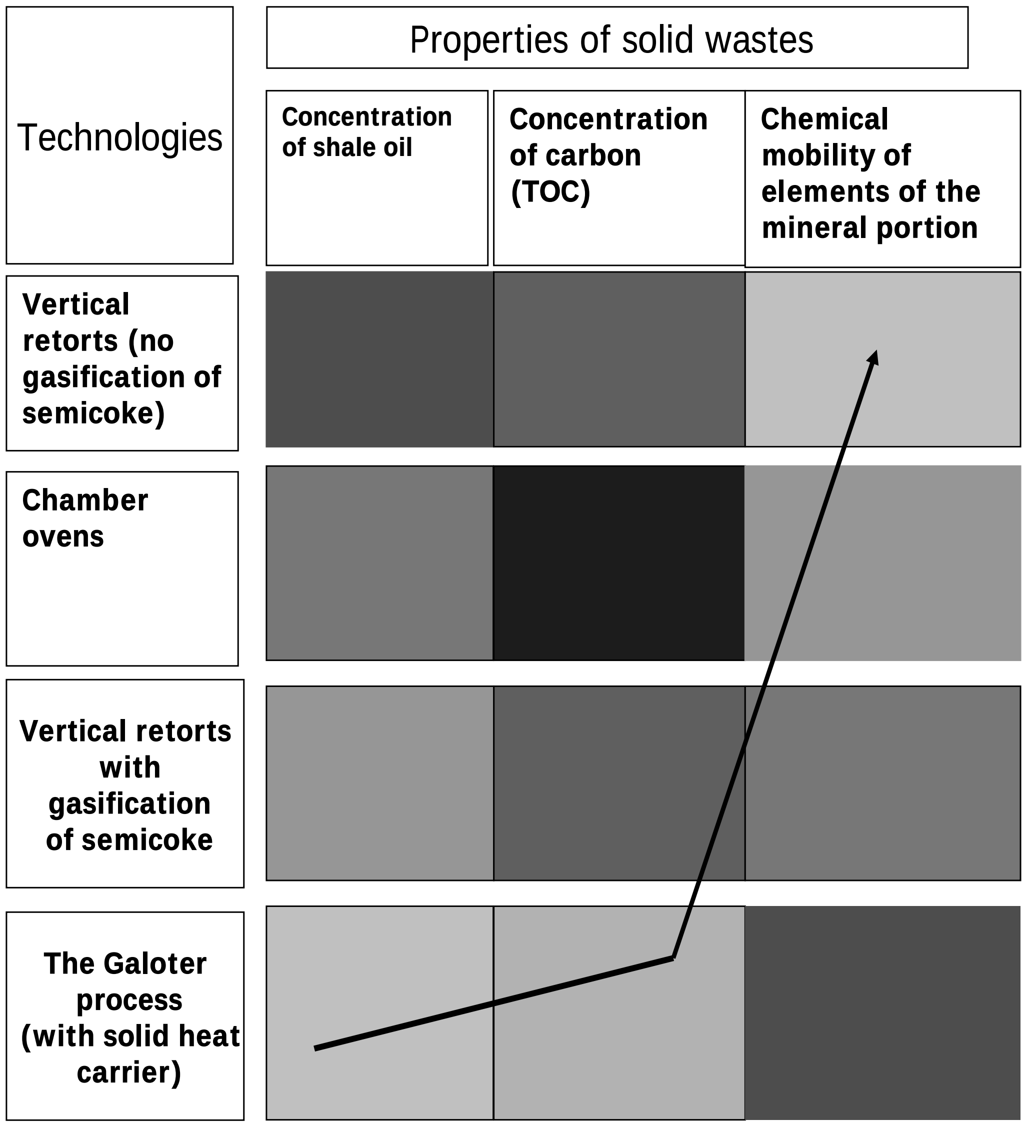


Figure 7: Ecology of oil shale processing

diagram that the maximum possible emission of organic components extracted from the solid wastes takes place when oil shale is processed by the retorts having no gasification of semicoke and the minimum may be observed in case of afterburning of semicoke with solid heat carrier.

At the same time the solid wastes produced by the retorting processes having no zone for semicoke gasification and the chamber oven coke (char) exhibit the highest concentration of carbon which indirectly indicates to the presence of polyaromatic compounds in the solid waste which belong to most hazardous environmental polluters.

At the same time, afterburning of semicoke by technologies with solid heat carrier leads to increased chemical mobility of elements of the mineral portion of oil shale. If oil shale has a high concentration of heavy metals and especially that of radioactive elements in its mineral portion, afterburning of semicoke may be connected with high ecological risks.

Ecologically favorable processing of oil shale is accomplished in vertical retorts with gasification of semicoke. However, running of such retorts proved technically difficult which led to closing of this type of retorts operated at that time in Estonia.

The arrow in the diagram indicates the presence of the optimum qualitative properties of solid wastes produced by oil shale processing.

During 2001-2006 solid wastes produced by vertical internally heated retorts and by processing technology with solid heat carrier were studied by TTU Institute of Oil Shale Research to reveal their conformity with the above criteria, but also the possibilities of improving the vertical retort technology for conditioning their solid wastes according to European requirements. The results of these studies are given in Table 1 and Table 2.

A comparative analysis indicates that the concentration of total organic carbon of the semicoke produced by vertical retorts several times exceeds the concentration of total organic carbon (TOC) of the ash produced by the process with solid heat carrier, besides if the vertical retort is operated according to the technological chart i. e. no air and gas is injected into the additional chamber, the concentration of oil in the semicoke exceeds 700 mg/kg.

## Conclusions:

1. *The accelerated development of oil shale processing in the future is possible if the requirements for ecological safety are met.*
2. *The ecological safety should be based on the development of technological methods ensuring complex utilization of oil shale resources.*
3. *From the point of view of international*

**Table 2: Results of experiments in vertical retort**

| | No gas injected into additional chamber | | | Gas injected into additional chamber | | | | Air and steam injected into additional chamber | | Air and gas injected into additional chamber | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Run no. | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 |
| Date | 09.07 | 13.08 | 21.08 | 10.07 | 11.07 | 12.07 | 24.07 | 14.08 | 16.08 | 22.08 | 24.08 |
| Oil | 0.74 | 0.79 | 0.70 | 0.02 | 0.02 | 0.08 | 0.51 | 0.00 | 0.10 | 0.50 | 0.00 |
| Semicoke | 96.60 | 97.32 | 95.70 | 95.52 | 96.03 | 96.18 | 94.27 | 97.29 | 95.13 | 95.88 | 95.85 |
| Water | 1.10 | 1.28 | 2.09 | 2.85 | 2.94 | 2.72 | 3.07 | 2.11 | 2.83 | 2.70 | 3.10 |
| Gas + losses | 1.57 | 0.61 | 1.51 | 1.61 | 1.01 | 1.02 | 2.15 | 0.60 | 1.94 | 0.91 | 1.04 |
| Gas, m3/t | 9.46 | 5.73 | 8.70 | 13.07 | 7.94 | 8.76 | 10.17 | 5.61 | 4.96 | 12.66 | 2.33 |
| Analytical moisture, % | 0.98 | 1.56 | 0.73 | 2.91 | 0.76 | 0.49 | 2.2 | 0.81 | 2.13 | 0.92 | 4.02 |
| Carbonchioxide (CO2)d, % | 11.62 | 6.85 | 6.48 | 6.39 | 6.54 | 7.90 | 7.17 | 9.02 | 5.12 | 7.95 | 7.47 |
| Ash, % | 71.04 | 83.68 | 87.86 | 81.06 | 81.20 | 82.40 | 81.55 | 82.10 | 86.58 | 78.96 | 84.26 |
| Organic matter, % | 17.34 | 9.83 | 5.66 | 12.55 | 12.26 | 9.7 | 11.28 | 8.88 | 8.30 | 13.09 | 8.25 |
| Total organic carbon (TOC), % | 3.270 | 3.550 | 3.040 | 2.710 | 2.400 | 2.490 | 3.230 | 1.950 | 1.260 | 2.490 | 0.980 |
| Total sulphur, % | 1.56 | 1.97 | | 2.41 | 2.38 | 1.70 | 2.20 | 2.05 | 2.78 | | |
| Calorific value, kcal/kg | 428 | 411 | 208 | 286 | 226 | 235 | 362 | | | | |

**Table 3: Concentration of hazardous substances in ash from the Galoter process**

| | | | Safe storage of solid wastes Specified by Council Directive 1999/31/EC | | | Ash from ash cyclones of the Galoter process | |
|---|---|---|---|---|---|---|---|
| | | | ISO | Inert | Hazardous | Runs with oil shale | Runs with oil shale and rubber |
| Concentration in solid wastes % wt | Total organic carbon, TOC | | 8245-1999 | ≤11) | ≤31) | 0.75 – 1.0 | 1.0 – 1.5 |
| | Total sulphur, Sdt | | EVS 664:1995 | Not specified | Not specified | 1.57-2.41 | 1.66-1.99 |
| | Sulphide sulfur, Sds | | EVS 664:1995 | Not specified) | Not specified | 0.78-1.49 | 0.99-1.32 |
| Concentration in aqueous eluates of solid wastes | pH, (-lg[$H^+$]) | | DP-10523 | 4.0-13.0 | 4.0-13.0 | 12.50-12.94 | 12.80-12.98 |
| | TOC, mg/l | | 8245-1999 | ≤200 | 40-200 | 80-170 | 75-180 |
| | Phenols, mg/l | | 6439-1990 | ≤10.0 | 20-100 | 1.96-6.80 | 1.96-6.20 |
| | Sulphetes, g/l | | DIS-9280-1 | ≤1,0 | 0.2-1.0 | 0.368-1.22 | 0.402-0.938 |
| | Chlorides, g/l | | DIS-9297 | ≤0.5 | 1.6-6.0 | 0.14 | 0.14 |
| | Ammonium, mgn/l | | 7150-1983 | ≤50.0 | 0.2-1.0г/л | 1.97 | 1.81 |
| | Nitrites, mg/l | | 6777-1983 | ≤3.0 | 6.0-30.0 | 0.021 | 0.2 |
| | Easily extractable cyanides, mg/l | | 38405-D14-88 | ≤0.1 | 0.2-1.0 | Not detected | Not detected |
| | Fluorides, mg/l | | DP-10359-1 | <5 | 10-50 | | |
| | Heavy metals mg/l | Pb | 8288-1985 | Total content of metals, ≤ 5 mg/l | 0.4-2.0 | 0.138-1.453 | 1.064-1.372 |
| | | Cd | 8289-1985 | | 0.1-0.5 | 0.014-0.093 | |
| | | Cu | 8288-1985 | | 0.1-0.5 | 0.0-0.044 | |
| | | Zn | 5666-1/3-89 | | 2.0-10.0 | 0.046-0.475 | 0.058-0.085 |
| | | Cr+6 | DIS-9174-88 | | 0.1-0.5 | 0.277-0.612 Crtotal | 0.0-0.472 Crtotal |

*ecological requirements, the future oil shale processing technologies providing deep conversion or afterburning of carbon and the organic mass of semicoke may be regarded as acceptable to date. As such processes may be considered those with solid heat carrier and vertical retorts with semicoke gasification.*

4. *Take into account that solid heat carrier process is more flexible in technological aspects, compare with vertical retort, the best available technology now is solid heat carrier process.*

5. *To provide systematic approach to the solution of problems of oil shale processing international cooperation in technological and ecological fields is needed.*