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ALTERNATIVE WAYS FOR USING OIL SHALE

The per capita production of oil shale in Estonia is higher than in any other country. Yet the oil-shale industry has achieved the volume of output which is long in conflict with both the oil-shale reserves left and the nature protection. The same applies to the oil shale-based power industry.

In such a situation one may wonder if it is expedient to search for new applications for oil shale. Probably yes and also the existing trends, viz. thermal processing and combustion, should be improved and supplemented by new ones.

This article considers possibilities of the non-fuel use of oil shale, especially powdered oil shale, organic matter concentrate, oil shale beneficiation residues.

In the deposit, oil shale seams lie alternately with limestone interlayers. The organic content of oil shale is 35 %, in some cases amounting to 70 %.

The oil shale mineral part consists mainly of calcite and clay minerals. 20--250 μm organic globules are surrounded by the mineral part. The mineral and organic parts differ in properties. This facilitates the selective concentration of kukersite and the use of the products obtained.

Oil Shale Enrichment

Methods of enrichment, including those of oil shale, may be conditionally classified as follows:
(1) mechanical
(2) physical (divided in turn into magnetic and gravity ones, and flotation)
(3) chemical
(4) biological
(5) combined methods

Mechanical concentration. By sorting out from the conveyer belt only high-grade oil shale and successively crushing it kerogen-50, i.e. organic matter concentrate with a 50 % organic content, may be relatively easily produced. A richer concentrate may be produced by crushing oil shale so that organic globules could be released from the mineral part possibly completely.

Mechanical processes enable concentrates with different organic contents to be obtained by properly choosing the crushers and sieves.

Gravity concentration. By industrial concentration of lumpy oil shale the pulsating water stream or powdered magnetic suspension is used which lifts oil-shale lumps of higher organic content to the surface. The method enables oil-shale lumps from the gangue (limestone lumps) to be separated. The organic matter globules (their specific gravity is 1,110, that of calcite 2,710 kg/m^3) released from the mineral part are separated from the mineral portion in heavy liquids, e.g. in an aqueous $CaCl_2$ solution or in the mixture of tetrachloromethane and benzene. Mainly aqueous solutions of mineral salts are used in industry and in order to accelerate the process, centrifuges are employed.

Flotation is based on the difference in physico-chemical properties of the oil shale particles surface. The air bubbles to be directed through an aqueous suspension of powdered oil shale stick to the organic particles coated with flotation reagents, rise together with them into the foam layer formed on the suspension surface and will be removed.

Chemical enrichment. The most widely known laboratory method is the treatment of oil shale alternately with aqueous solutions of HCl and HF. By means of the former carbonates are decomposed, while the latter decompose the other mineral substances, except pyrite.

If carbon dioxide is directed into the water suspension of oil shale under pressure, carbonates will be dissolved by the H_2CO_3 formed that enables oil shale to be subsequently enriched by physical methods.

Biological enrichment. Microorganisms, e.g. *Thiobacillus ferrooxidans*, may be used to remove pyrite from oil shale. The sulfuric acid formed by biological oxidation will partly dissolve also the oil shale mineral part.

In industry mainly physical enrichment methods are used.

On the History of Kerogen Production

In 1948 A. Rembashevskii, A. Konev and V. Proskuryakov, St. Petersburg, received a patent on the commercial production of kerogen. The world's first enrichment plant to obtain kerogen-70 was built at the Slantsy Integrated Plant, Leningrad Region (Russian Federation) in 1963. The output of flotoconcentrate was in the beginning 1,000 t/y, later about 11,000 t/y.

In 1964 R. Koch, E. Silver and V. Ahelik started preliminary works in the Institute of Chemistry, Estonian Academy of Sciences, under the direction of O. Kirret to obtain kerogen-90 by flotation. The results enabled the construction of a pilot plant at the Experimental Works of the said Institute to produce dicarboxylic acids and plant growth stimulator within the period of over ten years. At the same time, the flow chart of enrichment was supplemented (A. Kitsnik) by a flotocyclon, a special desintegrator and other innovations (specifications of kerogen production are presented in the Table).

The Use of Powdered Oil Shale and Kerogen as Filling Material

The gangue containing up to 10 % of organic matter (the mineral part consists mainly of calcium carbonate) replaces in powdered form baryte, asbestos, talk, chalk and kaolin in manufacturing floor coverings such as rubber linoleum, linoleum and polymeric plates. It is also used as filling material in rubber products and artificial leather, in producing mastics and polymeric cement.

The flotoresidues formed on producing kerogen-70 (more than half of the particles with a size below 50 μm) contain about 20 % of organic matter. Half of the mineral part is composed of calcite, the content of quartz and hydromica being 15 % each. It is used in polychlorovinyl linoleum, hermetic materials, mastics and porous linoleums, as a substitute for chalk and white soot in artificial leather.

Sludge consists of up to 110 μm particles, its organic content being 37 %. The mineral part is mainly composed of calcite, the content of quartz, orthoclase and

Technical parameters of production of kerogen concentrate

OM* content of concentrate, %	OM content of oil shale, %	Yield of concentrate, %	Extraction of OM into concentrate, %	Consumption of oil shale, t/t	Yield of concentration residue, t/t	OM content in residue, %	Method of beneficiation
70	33	24	52	4.2	3.2	21	Flotation, operating plant (1973)
70	35	31	62	3.2	2.2	19	Flotation (1973)
70	34	40	86	2.5	1.5	8	Flotation (1975)
70	39	48	88	2.1	1.1	9	Flotation (1975)
70	33	40	85	2.5	1.5	8	Centrifugal method, hydroseparation (1975)
70	39	47	86	2.1	1.1	10	Centrifugal method, hydroseparation (1975)
70	33	38	80	2.6	1.6	10	Centrifugal method, hydroseparation (1973)
79	36	40	82	2.5	1.5	11	Flotocyclone method (1980)
87	33	31	81	3.2	2.2	9	Combined (1978)
90	40	40	90	2.5	1.5	5	Flotation (1954)
90	40	40	90	2.5	1.5	7	Combined (1975)
90	31	31	81	3.3	2.3	9	Combined (1978)

*OM - organic matter

pyrite being less considerable. It is mainly used in the preparation of steel casting mixtures.

Powdered oil shale whose organic content is 5-50 % is a good filler in polyolefins-based products.

Kerogen-70 is a dark to light-brown powder, at least 98 % of which is able to pass through sieve No. 14. The density is below 1,350 kg/m^3, and moisture below 3 %. May replace ebonite powder in natural and synthetic ebonite, wood flour in thermoreactive compressing materials and alkyd linoleum, in the latter also cork flour.

Kerogen-90 may replace kerogen-70 as a filler in producing different materials. In most cases, with increasing organic content of the concentrate the product properties will be improved.

The specific surface of the **activated kerogen-70** processed in the desintegrator is up to 15 m^2/g and it is used as a light filler in rubber products, artificial leather and thermoplastics.

Nondusting kerogen differs from kerogen-70 in that it contains, depending upon grade, 10-18 % of petroleum oil or other softeners. It is used as a filler in technical rubber products and plastics, etc. but mostly in manufacturing accumulator monoblocks.

Mastic keralene is a mixture of altine-50 and kerogen-70 and is used as the water proofing of balconies, on connecting wall panels, in coating fastening parts, on constructing well roofs. The number behind the name (e.g. keralene-30) indicates the percentage content of kerogen-70.

Vinizol is a thermoplastic material obtained from polyvinyl chloride and kerogen-70. It replaces the preservative-treated wood and asbestos cement in preparing the fillings for water-cooling towers.

Keroplast is obtained from the same components and is used as lining in cooling towers, as well as industrial and civil engineering.

Kerelast is a polymer of a higher content of filler and is composed of kerogen-70 and latex. It is used in manufacturing technical rubber products and several other polymeric materials.

Minelast is produced like kerelast, enrichment residues being used as starting material.

The explosion and fire hazard of kerogen-70, kerogen-90 and kerelast may be reduced by adding antipyrenes, e.g. phenyl-naphthylamines.

The Chemically Modified Kerogen

The products obtained on chlorination and dehydrochlorination, sulfonation, amination, phosphorylation, epoxydation, thiocyanation and chloroxidation have been used as a filler of polymeric materials, as kationites, antipyrenes, vulcanization accelerators, epoxy resin hardeners, etc.

Synthesis of Dicarboxylic Acids and Plant Growth Stimulators

The technology for oxidation of kerogen-70 suspension with air oxygen at 175--200 °C in a 30 % aqueous solution of caustic soda at a pressure 30-40 atm has been worked out at the Slantsy Chemical Integrated Plant, Leningrad Region, Russian Federation. The previously filtrated reaction mixture is acidified with sulfuric acid. The polyfunctional acids precipitated by acidification are separated and neutralized with an alkali and the plant growth stimulator "Lentekhniin" is obtained whose technology of production has been developed at the Leningrad Institute of Technology. The aliphatic dicarboxylic acids present in the sodium sulfate solution are extracted and may be used to obtain polyurethane foam. The complete purification of acids is complicated due to the presence of oxygen compounds additives of complex structure.

According to the method developed at the Institute of Chemistry, Estonian Academy of Sciences, weak nitric acid is used as an oxidizer of kerogen-90 together with air oxygen at 140 °C at 5-7 atm. The polyfunctional acids are insoluble in acidic medium and are separable from the reaction mixture. A plant growth stimulator (CPB) may be obtained by neutralization of polyfunctional acids. It may also be produced without increasing pressure in the reactor, on oxidation at room temperature, using kerogen-90, kerogen-70 or powdered oil shale as starting material. Aliphatic dicarboxylic acids are purified by either distillation and recrystallization or rectification of their dimethyl esters. A mixture of pure acids or of their diesters, in case of need also succinic, glutaric, adipic, pimelic and suberic acids, may be produced. The mixtures of acids (containing diacids up to sebacic ones (incl.)) or their dimethyl esters are used for producing polyurethane foam and especially in manufacturing frostproof plasticizers (—60 °C). In the latter case, sebacic acid manufactured from castor oil, may be replaced by these mixtures.

The diacids serve as a starting material in fine chemistry. Succinic acid is also known as a plant growth stimulator.

Production of Feed Protein

In the early seventies there appeared several publications dealing with problems of the production of feed and edible protein from kerogen and its oxidation products in a microbiological way suggested by scientists of the Leningrad Institute of Technology.

The low-molecular oxidation products of the water suspension of kerogen-70 with air oxygen were considered to be most suitable starting material for biosynthesis as they do not contain mineral salts retarding the growth of microorganisms. Recently more attention has been paid to the use of mixtures of the organic acids obtained on kerogen ozonization. The drawback of the first method is the low acid yield, the expensiveness featuring the second one as kerogen will be subjected to ozonization in glacial acetic acid. The protein content of the yeast biomass obtained on using the oxidation products is 45, that of bacterial biomass 60 %. The oxidation products are also used as a lysine biosynthesis stimulator.

Carbon Adsorbents

In the U.S.A. a method has been found for rendering oil or oil products from the water surface using kerogen or its thermal processing residue. Kerogen-90 may also be used in producing mineral adsorbents from aluminium oxide as well as from lignin. High quality adsorbents may be produced by adding kerogen-70 to the filling mass consisting of coal powder and the tar obtained by chemical treatment of wood.

Oil Shale as Organic Mineral Fertilizer and Ameliorator

The favourable effect of oil shales on plant growth has been observed in case of Karelian shungite (metamorphosed oil shale), Moroccan, Yugoslavian, Hungarian and Azerbaijan, as well as Estonian oil shale and that of the Leningrad Region. There is no uniform opinion about the mechanism of action.

While in several places in the world oil shale has been started to use to raise soil fertility, then in Estonia we are forced to tackle the problem of utilizing the oil shale accumulated in dumps in northeastern Estonia and also in quarries at Maardu where it participates in the process of humus formation.

Perspective

Experience shows that powdered oil shale, oil shale organic matter concentrates and concentration residues may be used in producing different products.

One should consider the production of kerogen-90. The concentrate with such a high organic content has not been yet commercially produced in the world. Estonia is in this respect in a more favourable situation due to the better possibility of enriching local oil shale as compared to that of the Leningrad deposit.

Also the original developments of Estonian scientists and process engineers (Institute of Chemistry, Oil Shale Research Institute, etc.) in the field of oil shale concentration and utilization not introduced yet will also contribute to the launch of the new industry.

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