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Toxicity of oil shale chemical products

A review

by HUBERT KAHN, M.D.¹

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Deep within the earth enormous supplies of oil shale are deposited. Their importance is constantly increasing due to the depletion of high calorie fuels which can be mined more easily [crude oil (rock oil, petroleum) coal]. The world supplies of oil shale have not yet been completely inventoried, but in a calculation for oil shale tar they have been evaluated to amount to as much as 3.10^{14} t (30). The great future importance of oil shale as an energy resource and raw material for the chemical industry was emphasized at the Symposium of the United Nations Organization on Oil Shale Exploitation and Usage which took place in Tallinn in 1968.

Oil shale deposits have formed during all the geological periods from the Cambrian through the Tertiary. The United States, the Soviet Union, Brazil, Canada, and some other countries possess large oil shale deposits (table 1). Currently the greatest producer and consumer of oil

shale in the world is the Estonian Soviet Socialist Republic (Estonian S.S.R.) (24).

The primary chemical product of the thermal processing of oil shale kerogen is oil shale tar. It is a dark brown liquid with a characteristic smell. As to their physico-chemical characteristics, oil shale tars greatly differ from crude oil. Their characteristics also differ according to the location of the oil shale deposits (table 2).

In the Estonian S.S.R. a great variety of various products are currently produced from oil shale tars and phenols, e.g., fuel oil, oil for sleeper steeping, oil shale solvent, benzene, toluene, oil shale tannins,

Table 1. General potential supplies of oil shale calculated for oil shale tar in the world and in some countries.

Countries	Oil shale tar (million tons)
United States	24,600,000
Brazil	1,200,290
Soviet Union	195,310
Chinese People's Republic	24,500
Canada	23,500
All world resources	26,052,383

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various varnishes, glues, bitumens, electrode coke, rubber modifiers, "nerosin" for fighting wind erosion, etc. (6).

ANIMAL DATA ON THE TOXICITY OF OIL SHALE TARS

The first research on the toxic effect of oil shale tars was carried out at the Tartu State University (23). It proved that the application of oil shale tar to the skin of white mice causes various inflammations of the skin, degenerative changes in internal organs, and derangements of some physiological processes of the higher nervous system.

Depending on the thermal processing method used with the oil shale, the tars may have different physicochemical characteristics, and therefore they are not all toxic to the same degree (table 3). The real danger of poisoning in industry depends not only on the toxicity of a specific oil shale tar, but also on its volatility. For example, the average lethal concentration of tunnel tar (60 mg/l) is only twice as high as that of chamber tar (30 mg/l), but, since the volatility of tunnel retort tar is eight times higher than that of chamber tar, the real danger of intoxication with the former is considerably higher than with the latter (11).

The chemical composition of the volatile components of oil shale tars is not yet

known. In 1955 it was found that the volatile components of these tars invariably contain phenols and aldehydes (10). Later phenols were determined to be the primary toxic factor even though the whole complex of the volatile substances was found to be toxic (11).

At the same time, corresponding exposure studies have proved that dephenolated oil shale tars are toxic as well. Due to the chronic effects of the volatile components of these tars, moderate focal parenchymatous dystrophy and fine-grained toxic fatty degeneration may be observed in the liver of experimental animals. Their application to skin causes inflammation, and in short- and long-term exposures the volatile components of dephenolated tar cause various nonspecific symptoms of intoxication (12). Therefore it has been concluded that in the hygienic evaluation of the work environment it is not only necessary to consider the ambient air concentration of phenols but also that of hydrocarbons.

From the hygienic point of view, the ability of oil shale tars to enter the organism, even through unaffected skin, and their marked general resorptive effect must be remembered (15).

Independent of the route of entry of oil shale tars into the organism, the symptoms of intoxication in experimental animals are similar and reveal the neurotrophic effects of these substances, e.g., incoordination, clonic and tonic convulsions, paresis and paralysis of the extremities, narcosis. In cases of long-term exposure changes occur in other organs and systems as well. For example, symptoms of anemia and leucopenia have been observed in experimental animals, as well as a decrease in the activity of the oxidation-rehabilitation ferments of catalase and peroxidase, a reduction in the content of the sulfhydryl groups, and a decrease in the serum glucose level. It has also been ascertained that oil shale tars oppress the antitoxic and protein-forming functions of the liver, i.e., the duration of hexenal narcosis is longer in intoxicated animals than in controls, the quantity of albumin in blood serum is reduced, etc. (6).

Oil shale tars impair kidney function as well. The content of residual nitrogen

Table 2. Comparative data on oil shale tars and crude oil (rock oil, petroleum).

Characteristics	Oil shale tars		Crude oil
	Estonian S.S.R. (Kukersite oil shale)	United States	
Heat production (kcal/kg)	9,500	10,000	10,400—11,000
Content of oxygen compounds (%)	50—60	10—20	to 5
Among these phenols (%)	20—30	2—3	to 2

Table 3. Comparative toxicity of oil shale tars and phenols in the Estonian oil shale deposits.^a

Products	Method of processing	Main forms of usage	LC ₀ (mg/l)	LC ₅₀ (mg/l)	LC ₁₀₀ (mg/l)	LD ₀ (mg/kg)	LD ₅₀ (mg/kg)	LD ₁₀₀ (mg/kg)
Generator tar	Dry distillation or half-coking of oil shale in mine gas generators	Oil for wood-steeping and for production of electrode coke, phenols, astringents, etc.; a means for increasing crop capacity and fighting wind erosion of soils	13.0	27.3 ± 0.2	30.0	5,000	10,400 ± 350	12,000
Chamber tar	Oil shale coking in chamber retorts which are meant for the production of household gas	Production of electrode coke, oil for woodsteeping, pure aromatic compounds, etc.	18.0	39.4 ± 0.4	45.0			
Tunnel tar	Dry distillation and half-coking of oil shale in tunnel retorts	Production of benzene, phenols, electrode coke, oil for woodsteeping, fuel oil	54.0	66.0 ± 2.0	76.0			
Tar of the device with a hard heat carrier	Half-coking of oil shale in the device with a hard heat carrier	Production of oil for woodsteeping, benzene, bitumens, boiler fuel, detergents (sulfanol, timol)						
Light fraction			55.0	63.3 ± 3.0	99.0	4,200	900 ± 150	13,000
Average heavy fractions			7.0	16.2 ± 2.0	24.0	—	—	—
Diesel fraction of oil shale tar	Of the mixture of tars of half-coking	Production of oil shale phenols, phenolates, oil for sleeper-steeping	14.0	15.5 ± 0.3	18.0	1,100	5,800 ± 300	13,500
Nondephe-nolated oil shale tar	Mixture of tars of oil shale half-coking	Sleeper-steeping, production of electrode coke, etc.	14.0	16.5 ± 0.27	18.6	1,100	5,800 ± 300	13,500
Dephenolated oil shale tar	Mixture of tars of oil shale half-coking	Raw material for tar products	12.0	19.5 ± 0.43	22.0	2,200	10,000 ± 400	18,000
Oil shale phenols of subtar water (water-soluble phenols)	Of subtar waters	Main raw material of oil shale chemical synthesis, production of synthetic tannins and glues	—	1.95 ± 0.62	—	400	765 ± 70	1,000

^a LC = lethal concentration; LD = lethal dose.

in blood increases, and albuminuria, ketonuria and glucosuria may be observed. The excretion of free phenols in urine and their rate of entry into internal organs (liver, kidneys, spleen, brain, heart) increases. An increase in the combined phenols in internal organs also occurs, a fact which, according to Bidnenko (4), shows their participation in the detoxication processes of the main toxic component of oil shale tars.

The changes caused by oil shale tars in internal organs have been confirmed morphologically. In liver, kidney, heart, muscle, brain and cerebellum tissues dystrophic changes have been observed, and in spleen tissue changes characteristic of

the depression of lymphocytopoiesis have been found.

The sensitizing effect of oil shale tars on the organism has been shown in animal experiments. Epicutaneous application tests on guinea pigs have caused allergic reaction of the delayed type by Sooks (15).

On the basis of recent animal experiments it seems as if oil shale tars have a gonadotrophic effect because they cause derangement of the estrous cycle in experimental animals (14).

During a four-month administration of generator oil shale tar in a dose of 0.1 g/kg daily, a decrease in the quantity of normal spermatogones in the sperm-producing epithelium of the testes of

white rats was observed. As the same dose produced no general toxic effects (according to the results of the same study), oil shale generator tar may have a specific gonadotrophic effect (16).

ANIMAL DATA ON THE TOXICITY OF OIL SHALE PHENOLS

The toxic effect of oil shale phenols is determined by the combined effect of their components. In the case of inhalation the volatile components are responsible, while application to the skin involves the whole complex of components. Seventeen individual representatives of phenols, mainly the derivatives of 5-alkyl-resorcin (up to 75 %), have been identified, by means of gas chromatography, in the volatile components of water-soluble oil shale phenols condensed from an exposure chamber (5).

Akkerberg and Jürgenson (1) showed that oil shale phenols are considerably more toxic than the phenols of coal distillation. The absolute lethal concentration of coal tar phenols for white mice is 5.6 mg/l, while the corresponding concentration of oil shale tar phenols is 0.2 mg/l and that of the subtar water phenols is 0.46 mg/l (table 3).

Blinova et al. (6) found that the threshold concentration of oil shale phenol vapors in acute exposures of rats was, according to the change in the cumulative threshold index, 0.2 mg/l, while concentrations of 0.1 mg/l and 0.03 mg/l had no effect.

Oil shale phenols, at a concentration of 0.03—0.05 mg/l (five times weekly, 4 h daily for six months), have caused the following disorders in experimental animals during prolonged inhalation: the syndrome of neuroendocrine derangement with inhibitory processes in the central nervous system, a reduction in the functional activity of the thyroid gland, exhaustion of the available and potential resources of the glucocorticoid function of the adrenal cortex.

Animal experiments have shown that subliminal concentrations of oil shale phenols affect, first of all, the central

nervous system and endocrine organs (5, 6); this finding was true also for the single representatives of oil shale phenols. For example, Veldre (38, 40) found that due to small doses of cresol, naphthol and 5-methyl-resorcin, as well as due to the combined effect of p-cresol and β -naphthol, the relative reflex activities of white rats are the most sensitive indicators.

Studies on the toxic effect of the volatile components of oil shale tar phenols have proved that the symptoms of intoxication in inhalation proceed in much the same manner as the effect of a narcotic substance, i.e., excitement, intermittent inertia, staggering gait and a lateral position of the body have been observed in animals (6). The investigations proved that oil shale phenols irritate the skin and, if the effect is prolonged, they even cauterize it (3, 13). The repeated application of oil shale phenols to experimental animals caused seroexudative contact dermatitis and, in greater concentrations, necrosis of skin integuments.

In a single exposure of the tails of white mice to oil shale phenols the following symptoms of skin absorption were observed: inertia, dyspnea and incoordination, lateral position of the body, and death of some mice (1). It has been proved that oil shale phenols may enter the organism through unaffected skin and that they cause intoxication with clearly expressed symptoms resembling those caused by phenols with an origin other than oil shale (3).

CARCINOGENICITY OF OIL SHALE CHEMICAL PRODUCTS

The honor of being the initiator of research on the carcinogenicity of oil shale chemical products belongs to Prof. Bogovski. This work, performed under his leadership, has proved that all primary products of the thermal processing of Estonian oil shale have a blastomogenic effect. The higher the processing temperature, the more evident the carcinogenic activity of oil shale tars. The dephenolation of chamber tar increases the carcinogenic activity of this product (7). In 1972

data on the carcinogenic activity of oil shale tars in CC₅₇BP mice were published. The results of that study showed that generator tar caused skin neoplasms in 48.5 % of the animals, the tar of the device with a hard heat carrier in 36 %, and tunnel retort tar in 35 % of the animals exposed (41).

Although the carcinogenic characteristics of oil shale phenols still need more study, Mirme (29) has proved that water-soluble oil shale phenols are cocarcinogenic substances. Studies of the work environment of oil shale processing plants have shown the permanent presence of benzo(a)pyrene in the air, although the values did not exceed the maximum allowable concentration (15 mkg/100 m³) (2). For example, at the work sites of chamber retorts the benzo(a)pyrene content fluctuated from 0.25 to 5.8 µg/100 m³, and on the loading trestle bridge of the shale oil device it varied between 0.75 and 3.78 µg/100 m³. The benzo(a)pyrene content in the sewage of the oil shale processing industry may reach high concentrations, from 0.002 to 0.02 mg/l and even to 0.1 mg/l. But after sewage disposal (coagulation-filtration-chlorination) the benzo(a)pyrene content is reduced to 11.6—17 % of the initial level (39).

Despite the fact that oil shale tars and oil shale bitumens have been shown convincingly to be carcinogenic, not a single case of occupational neoplasms in persons exposed to oil shale chemical products appears in the literature. Such a divergence in the results may be explained by the facts that (a) the results of animal exposure may only relatively be extrapolated to humans and (b) people systematically wash oil shale products from their skin and such washing is not usually applied in animal exposures. Finally, for the formation of malignant neoplasms in humans, exposure to carcinogenic oil shale chemical products must be prolonged (for decades).

At the same time it should be noted that in the most recent studies (9), which have used person-years as a basis for the calculations, a statistically significant ($p < 0.05$) excess morbidity for skin cancer among workers who have been employed in the oil shale processing industry for ten

years or more has been observed when compared with that of the general population.

EFFECT OF THE MAIN OIL SHALE CHEMICAL PRODUCTS ON THE HUMAN ORGANISM

In the literature, data appear on the irritating and sensitizing effect of oil shale tars on skin integuments and on the mucous membranes of the respiratory tract (26, 27, 28, 36). Loogna (25, 26) proved that oil shale tars may cause various skin diseases, i.e., contact dermatitis, folliculitis, warts, and vitiligo-like dermatosis. Oil shale tars also have slight sensitizing characteristics in addition to their local irritating effect. In industry, exposure to tars causes occupational allergic diseases, e.g., allergic dermatosis, chronic eczema, bronchial asthma. In some practically healthy people exposed to oil shale tar an "occult" sensibilization has been observed.

Histaminopenia and serotoninopenia indices were lower in persons exposed to oil shale tars, especially in workers with occupational dermatosis (26). Studying the effect of oil shale phenols on skin integuments, Majass drew the conclusion that these products contribute to the pathophysiological and biochemical derangements of the epidermoid barrier of the skin.

The general toxic effects of oil shale chemical products on the human organism have been studied for many years by the present author and his research group (18—22). The results of these investigations have shown that a considerable number of the persons exposed to oil shale tars, oil shale phenols and other oil shale chemical products experience the following symptoms: derangements of the central and autonomic nervous systems, peripheral blood, and biochemical parameters (increase in the excretion of free and total phenols, sulfates, glucuronic acid with urine; a rise in the activity of aminotransferases in blood serum), as well as a decrease in the immunologic resistibility of the organism. The frequency of subjective derangements and the excretion of phenols

Fig. 1. Comparative data on complaints experienced by workers occupationally exposed to oil shale tars and phenols and by a control (reference) group.

in the urine of persons exposed to oil shale tars and oil shale phenols in comparison with the appearance of the same parameters in a reference group is shown in fig. 1 and table 4.

Examinations of large cohorts of oil shale chemical workers have not revealed any cases of occupational intoxication. Still, in 35 % of those examined, subclinical dysfunctions were found, namely, vegetative dysfunction, asthenic symptoms or an asthenovegetative syndrome. Furthermore moderate changes in the blood picture (increase in the erythrocyte, leucocyte and thrombocyte counts) occurred in connection with changes in some biochemical parameters (increased content of phenols, glucuronic acid and organic sulfates

in urine) (20). Similar data have been published by Bidnenko (4), who studied the effect of "nerosin" (mixture of some fractions of generator oil shale tar) on workers' health. He noted that, apart from the subjective derangements of the central nervous system, a drop in body temperature and arterial blood pressure was observed. In workers exposed to oil shale phenols, tachycardia (in 23.0 % of cases), rapid orthostatic pulse (in 37.5 %), and changes in clinostatic reflex (in 32 %) were frequently observed (32). Some changes in microcirculation had been revealed. Spasm and spastic atonia of the capillaroscopic picture occurred in the hands of 10.3 % of the cases, in the legs of 11 %, and in the conjunctivas of 18 % (33).

Attention should also be paid to the clearly expressed individual differences in the sensitivity of people to oil shale chemical products. While some workers experience various derangements during the first years of occupational exposure to toxic substances (though usually not clearly expressed), others do not show a negative effect until their length of service has exceeded ten years (17).

THE OIL SHALE CHEMICAL INDUSTRY AND ENVIRONMENTAL PROTECTION

Large oil shale chemical plants which process millions of tons of oil shale every year undoubtedly pollute the environment through the emission of chemicals into the air and industrial sewage. The great content of nonvolatile phenols is character-

Table 4. Comparative data on the excretion of phenols in the urine of workers exposed to oil shale tars, workers exposed to oil shale phenols and a reference group.

Excretion	Reference group		Exposed workers					
			Oil shale tars			Oil shale phenols		
	N	Mean $\pm$ SD	N	Mean $\pm$ SD	p	N	Mean $\pm$ SD	p
Free phenols	100	91.6 $\pm$ 23.4	134	185.0 $\pm$ 23.5	< 0.05	174	192.0 $\pm$ 24.4	< 0.01
Total phenols	100	158.8 $\pm$ 12.8	134	243.0 $\pm$ 32.0	< 0.01	174	245.0 $\pm$ 32.0	< 0.01

istic of the sewage of oil shale processing (70—80 % of the total amount of phenols as compared to the 40—50 % in coke chemical sewage). Furthermore, the sewage contains oil shale tars, ammonia, 3,4-benzo(a)pyrene and some other chemical substances. The results of analyses have revealed that their pollution with organic substances is high. The oxidization of the water from general sewage emission fluctuates between 2.3 and 4.1 g/l (37).

As a result, sewage from the oil shale chemical industry harmfully affects the quality of the water in rivers, and it disturbs the normal process of self-purification in the water reservoirs. Still, during the last ten years a number of improved purification devices, methods and systems have been devised and introduced so that the pollution of water in reservoirs has decreased considerably. For example, due to the purification of phenol waters of benzo(a)pyrene (table 5), a considerable decrease in the content of benzo(a)pyrene has recently been observed in the small rivers of the Estonian oil shale fields when compared to 1972—1973. Now the benzo(a)-pyrene content does not exceed hygienic standards (0.005 $\mu\text{g/l}$) (35).

Data are available on the pollution of the atmosphere in areas near oil shale chemical plants. In analyses of the air at a distance of 2,000 m from one oil shale processing integrated plant, the following concentrations of toxic substances were found: phenols 0.4—0.5 mg/m³, benzene 1.0—2.5 mg/m³, toluene 2.5—3.5 mg/m³ (42). Studies on the content of harmful substances in the atmosphere due to the processing, storage and use of some liquid oil shale products (solvent, bitanol, shale oil "Ligno," etc.) revealed the main pollutants of air to be low aromatic hydrocarbons (31).

There are only a few papers dealing with the effect of the pollution of the atmosphere by harmful substances of the oil shale chemical industry on the health of the population. According to Etlin (8), the harmful substances of this industry have a considerable effect on the health of the population living at the distance of 400—1,000 m, and this effect is evident even in the case of a comparatively favorable location of a town in relation to the

Table 5. Effect of the phenol water disposal of BP at the oil shale processing integrated plant "Kohtla-Järve."

Water	Content of BP (mg/l)
Before dephenolation	68.0
After dephenolation	2.0
Before biological purification	0.16
After biological purification	0.12
After biological ponds	—

industry. The effect is seen in the slowness of development of children (up to the age of one year) and in an increased morbidity of diseases of the respiratory tract in children of an older age.

In spite of the fact that pollution problems still exist, it may be said that there is a constant tendency towards improvement. At present, new possibilities for oil shale usage without environmental pollution are being explored (34).

AIMS OF MEDICAL RESEARCH IN THE OIL SHALE CHEMICAL INDUSTRY

Different aspects of occupational medicine in the oil shale chemical industry have been studied systematically and purposefully during almost the entire postwar period. The leading role in this necessary and labor-consuming work belongs to the Institute of Experimental and Clinical Medicine of the Ministry of Health of the Estonian S.S.R., which is situated in Tallinn. It may be said without exaggeration that the research performed by this institute is really unique from the point of view of occupational hygiene, toxicology and occupational pathology. This research may become even more valuable when the oil shale industry expands in various countries throughout the world.

Still, it would be wrong to consider the medical research in this field as being complete. There are two main reasons which make the continuation of research in this field necessary, namely, (a) new oil shale chemical products are being pro-

duced and the main thermal processing systems for oil shale are being improved and (b) it is necessary to study the effect of oil shale chemical products on the human organism and on other biological subjects more thoroughly and from different viewpoints. Attention should primarily be paid to research on the remote consequences of small concentrations of oil shale chemical products on the human organism and to environmental protection.

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