Volume 8: Health Effects of Oil Shale Development

Western Oil Shale Development: A Technology Assessment

February 1982

Prepared for the
U.S. Department of Energy
Assistant Secretary for Environmental
Protection, Safety, and Emergency
Preparedness
under Contract No. DE-AC06-76RLO 1830

DOE Project Manager: G. J. Rotariu

Pacific Northwest Laboratory
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Pacific Northwest Laboratory Richland, Washington 99352

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FOREWORD

The U.S. Department of Energy (DOE), Office of the Assistant Secretary for Environmental Protection, Safety, and Emergency Preparedness (EP), Office of Environmental Assessments, has been conducting technology assessments of the evolving energy technologies. The purpose of these is to evaluate in as quantitative a manner as possible the potential environmental, health, and socioeconomic impacts of each technology as it moves towards commercialization. The assessments identify where further information is needed, provide an analysis of potential environmental, health, and socioecomonic consequences of each technology, and define research and development (R&D) needed to ensure environmentally acceptable commercialization.

This is the final report of the Western Oil Shale Development Technology Assessment. We would like to express our appreciation to Drs. Darryl Hessel and Ira Levy of the Pacific Northwest Laboratory for their efforts in coordinating the work, to Dr. Hessel and Mr. Gabor Strasser for preparing this report, and to the entire team of participants listed in the Executive Summary and in the Appendix of Volume 1 of this report for conducting and reporting the major technical studies.

Dr. George J. Rotariu Oil Shale Technology Assessment Project Manager Technology Assessments Division

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INTRODUCTION

Information on the potential health effects of a developing oil shale industry can be derived from two major sources: 1) the historical experience in foreign countries that have had major industries and 2) the health effects research that has been conducted in the U.S. in recent years. Both are valuable because the recent work applies modern scientific approaches to many of the generic questions while the experience in foreign countries offers more data on the long-term results of human exposure. The information presented here is divided into two major sections: one dealing with the experience in foreign countries and the second dealing with the more recent work associated with current oil shale development in the U.S.

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SUMMARY OF HEALTH EFFECTS COMPARISONS

Most of the health research currently under way in the U.S. is focused on site-specific concerns with major emphasis on analytical procedures, predictive modeling and toxicological experimentation. The opportunity to obtain meaningful epidemiological data will have to follow a significant scale-up of the U.S. industry. While similarities exist among the health impacts of oil shale development in various countries, there are crucial differences that preclude making judgments on the potential effects of a highly developed U.S. industry. From a study of both the historical evidence and the results of current research, several observations can be made:

- 1) Most of the current and historical data from foreign countries relate to occupational hazards rather than to impacts on regional populations. It is logical that current research in the U.S. should be focused first on occupational health concerns since the industrial population will be the earliest and most heavily affected, however, analyses based on effluent data from pilot-scale operations should be used to predict regional health impacts.
- 2) Neither the historical evidence from other countries nor the results of current research have shown pulmonary neoplasia to be a major concern, however, certain types of exposure, particularly such mixed source exposures as dust/diesel or dust/organic-vapor have not been adequately studied and the lung cancer question is not closed.
- 3) The industry should be alert to the incidence of skin disease in the industrial setting, however, automated techniques, modern industrial hygiene practices and realistic personal hygiene should greatly reduce the hazards associated with skin contact. The industrial practice of hydrotreating the crude shale oil will diminish the carcinogenic hazard of the product, however, the quantitative reduction of biological activity is dependent on the degree of hydrotreatment. Both Soviet and American experimentalists have demonstrated a correlation between carcinogenicity/ toxicity and retorting temperature; the higher temperatures producing the more carcinogenic or toxic products.
- 4) The entire question of regional water contamination and any resultant health hazard has not been adequately addressed. None of the countries

with industrial experience in oil shale have reported overt health hazards from water deterioration, however, the extraction techniques, the
geohydrology and the scale involved in a mature U.S. industry are not
comparable to either the Soviet or British conditions. Neither the
British nor the Soviet governments conducted (or are conducting) major
studies dealing with impacts on regional waters. It cannot be assumed
that no such impacts occurred.

FOREIGN EXPERIENCE WITH HEALTH EFFECTS OF OIL SHALE

Oil shale has been used as a source of energy and liquid products in a sustained manner in only two areas of the world: Great Britain and Estonia. The recent Brazilian industry provided no significant production until mid-1972 when the first Petrosix retort was completed.(1) Of the three foreign countries intermittently involved in shale oil production, the Soviets (Estonia) offer the most in the way of significant experimental and epidemiological data. The Scottish experience is historically important because of its impact on the general field of industrial hygiene and occupational medicine.

Because the Brazilian industry is new it will not be examined here. The major emphasis of this analysis will be placed on the Estonian effort followed by a summary of the major problems identified by the experiences in Great Britain.

OIL SHALE-RELATED HEALTH EFFECTS OBSERVED IN THE U.S.S.R.

History

The Soviet oil shale industry is the largest currently active one in the world. Development of the resource has taken place in a nearly continuous fashion under three governments. Beginning in 1920, Estonia began a research effort which resulted in the development, after 5 years, of a so-called Pintsch retort which produced town gas. This 200-ton-per day facility became the basis for the Kiviter gas generator currently in use in the Estonian SSR. In 1939 Estonia was taken over by Russia and then occupied by Germany as part of the general invasion of all Soviet territories in 1941. At that time the Estonian industry had reached over 800,000 tons per year. As the Russians retreated, they dismantled the industry and while the Germans planned an expansion, very little production took place before Russia regained the area in 1944. Apparently the reconstruction of the industry moved slowly until the refinement of the Kiviter process and the development of the Galoter process took place in the early 1960's. Historically, the principal use of Estonian shale has been for the production of low-BTU town gas and for direct combustion in

power generating plants.(2 & 3) Vosamae mentions the use of oil shale (as a solid fuel) in domestic stoves and furnaces.(4) It is probably that this private use of shale has been common far longer than there has been an industry. The use of Baltic or Estonian shale for the production of liquid fuel or chemical feed-stock has been a comparatively recent development, beginning in the early 1970's. It is important to recognize that both the Soviet shale and the extraction methods applied to it differ in significant ways from the U.S. resource and technologies.

Description of the Soviet Resource

The Baltic or Estonian shales are known as kukersite, and are extremely rich in recoverable organic components. Most Estonian ore assays more than 40 gallons/ton and is located very near the surface.(5) Kung describes the chemical analysis of kukersite and states that organic constituents account for 37% of the total.(6) Green River shales from the intermountain region of the U.S. average 25 gallons/ton or less and about 16% organic complexes.(7) Kung further states that Estonian shale is 13% SiO₂ of which 42% is in the form of quartz. Thus, quartz contributes only about 5.5% of the minerals, considerably less than the 15% found in the Mahagony zone of U.S. shales. The amount of silica present as quartz is an important factor in the development of the fibrotic and obstructive lung diseases often associated with mining industries.

The rich oil shale deposits are located in the northeastern part of Estonia very near the current border with Russia and about equidistant from Leningrad and Tallinn. The major industrial town of Kohtla-Jarve is at the approximate center of the oil shale region. The countryside is typical of a low coastal area, with numerous lakes, rivers and small swamps. Located at nearly 60° north latitude, the terrain resembles the lake region of northern Minnesota (author, personal observation). The depth of the shale rock is variable but probably averages less than 100 feet with some areas having an over-burden of less than 25-30 feet.

Two types of mining are carried out: strip mining in the shallower regions and underground mining in the deeper areas. Apparently in situ techniques have never been tried, either because of ready accessability of the shale or because it occurs in an alternating seam pattern. Strip mining is accomplished with large machinery and the shale rock is

transported to processing plants by both truck and train. Restoration of terrain and reforestation are practiced but the extent of this effort is not known. The underground mine "Estonia," located near Kohtla-Jarve, is probably the largest in the country and consists of a series of very long major drifts (up to 2-3 miles) served by an extensive lateral drift system. The dimensions of the rooms and drifts are considerably smaller than those found in U.S. oil shale mines and there is more evidence of constructed roof support systems. Apparently all underground equipment is electrically powered (author, personal observation).

Energy Production Technologies (USSR)

It should be emphasized that until very recently the main use of Baltic shale has been for direct combustion in power generating stations and for the production of low-BTU town gas.(8) Gas and oil production has been carried out in tunnel ovens, solid-heat-transfer retorts, and chamber ovens.(9) Tunnel ovens which are a variation of a moving grid system are the oldest of the Soviet technologies and are apparently still in limited use. The tunnel oven approach uses a train of hopper cars, loaded with shale, which are drawn through a long tunnel where hot gases are passed through the shale driving off the oil vapors and gas.(10) The solid-heat-transfer process is called the Galoter retort and closely resembles both the TOSCO II and the Lurgi-Ruhrgas retorts. Spent shale is used as the heat-carrier agent. The older Kiviter process (chamber oven) is similar in function to the Gas Combustion, Paraho, Petrosix and Union retorts. Both the Galoter and Kiviter processes are available in the U.S. under license from Resource Sciences Corporation of Tulsa, Oklahoma.(11)

In general, the modern oil and gas producing plants in the Estonian SSR combine the Kiviter and Galoter techniques since each process requires a different size shale, the former utilizing a feed-stock ranging from 1 to 5 inches while the latter requires fines up to 1 inch in diameter. A combined screening and flotation process separates the ore according to size after crushing (author, personal observation). An increasing proportion of the industrial population is employed in plants employing one or both of these techniques.

It should be noted that epidemiological data presented later in this report make no distinction among the several recovery techniques utilized

in Estonia, and that it is likely that workers are included who were exposed to more than one process including the direct-combustion power generating operations.

Experimental Results (USSR)

<u>Direct Toxicity.</u> Veidre and Janes reported on the relationship between boiling point, volatility and toxicity of several shale oils and selected fractions.(12) In general it appeared that those oils or fractions which originated from low temperature extraction processes or were marginally volatile at low temperature were the least toxic of the materials tested. The most toxic material tested was the diesel oil fraction. In this same article the authors make an unequivocal statement that the activity of the phenols determines the toxicity of Estonian shale oil. In both acute and chronic toxicity experiments the symptoms described are attributable to disturbance of the central nervous system. Long-term exposure led to a variety of systemic changes including anemia, leukopenia, reduction in blood glucose levels and changes in certain liver and kidney functions. Long term oral exposure (0.1 g/kg/day) of rats resulted in a decrease in primordial ovarian follicles in females and a reduction of normal spermatogonia in males.

Veldre states that no correlation exists between the toxic and carcinogenic properties of any of the shale oil materials tested. She further states that many of the products resulting from the use of shale oil as a petro chemical feedstock possess toxic potentials that are not necessarily different than those derived from other basic organic fuels. Soviet experimentation has led to the conclusion that the intensity of the skin effects of these end-use products correlates with the degree of inhalation toxicity.

In another report, Blinova classifies the oils from the various retorts according to their skin irritating effect. He found the oils produced at higher temperature (generator, chamber oven and tunnel oven) were more irritating than oil from the lower-temperature solid-heat-transfer system (Galoter process).(13)

<u>Carcinogenicity.</u> The Soviets have studied the carcinogenicity of oil shale products since 1951.(14) Bogovski has been the principal experimenter in the field and published a book on the subject in 1961.(15)

The major conclusions he draws from his experimentation are: 1) Higher carcinogenic activity occurs in the products resulting from higher temperature processing; 2) Benzo(a)pyrene (BaP) is a major factor in the enhanced carcinogenicity of many but not all, of the products and their fractions; 3) Aliphatic hydrocarbons may potentiate the carcinogenic effects of the aromatic compounds. The preoccupation with the presence of BaP in shale oil products led to assumptions by early experimenters which have since proven to be misleading. Bogovski reports the identification, by Eisen in 1959, of other known or suspected carcinogens such as 1,2-benzanthracene and 2-methyl-benzanthracene in shale oils. Some of these materials were low in BaP content and proved to be highly carcinogenic in experimental animals.

Vosamae studied the carcinogenic effect of oil shale ash, or soot, resulting from either direct combustion of kukersite or from combustion of Mazut (fuel oil). Benzene extracts of both materials were used and the results indicate that the soot resulting from direct combustion of kukersite showed a marked carcinogenic action and that the extract of soot from oil shale fuel oil was carcinogenic but that the effect was considerably less than that of the direct combustion material. These experiments emphasized the unreliability of BaP content as a measure of carcinogenicity since the fuel oil soot, which was less carcinogenic, contained the most BaP (1200 ppm) while the more carcinogenic direct combustion soot contained less (14 ppm).(16)

Vosame also performed intratracheal experiments in rats to determine the carcinogenic action of the various solid materials and their extracts in the lung. She could not demonstrate a significant increase in lung neoplasia over the incidence in controls for any of the solid materials. When tars derived from solids, were instilled under conditions that favor the penetration of tissues by carcinogens (i.e., in detergents) a nearly 50% incidence resulted.

While Veldre(17) found that, besides process temperature, the phenolic content of the products and by-products was an important factor in direct toxicity, Bogovski(18) was unable to demonstrate serious carcinogenesis attributable to the phenols found in shale oil or certain of its products. He used both direct (single stage) testing and promotion (two stage) schemes.

<u>Summary.</u> In summary, the Soviet experimentalists have defined the biological activity of most of the materials associated with the Estonian oil shale industry. They draw several major conclusions from their years of experimentation:

- 1. Direct toxicity is more pronounced with higher process temperatures and also to a lesser extent with degree of volatility.
- 2. Direct toxicity can be approximately estimated from the phenol content.
- 3. The intensity of skin effect correlates with the degree of inhalation toxicity.
- 4. Higher process temperatures produce more carcinogenic products and by-products.
- 5. Benzo(a)pyrene has been identified as an important carcinogen in many products and by-products and the Soviets appear to regard it as the ultimate measure of carcinogenic potential. Their data, however, conflict with this view and indicate that the presence of B(a)P alone is not a reliable indicator of carcinogenic activity.
- 6. The solid wastes (soot) possess carcinogenic properties which depend on whether they derive from directly burned shale ore or from shale fuel oil.

Effects on Worker and Regional Health (USSR)

The Soviet experience with management of industrial health problems related to an oil shale industry is the most extensive one that extends into modern times. Purde and Rahu(19) have published some findings related to cancer incidence in the Estonian oil shale region. They report that the incidence of stomach and lung cancer is higher than that found in the general population of Estonia but attribute this increased incidence to migration into the industrial district from other Republics in the U.S.S.R. Apparently over 70% of the Kohtla-Jarve stomach cancer patients have immigrated from areas where stomach cancer incidence runs 1.6-2.5 times higher than that of native Estonians. However, in this same study they cannot explain the high incidence of gastric cancer in the rural populations of the same district (low migration factor). Veldre has found that analysis of water, soil and vegetables for BaP was not significantly different from control (non-oil shale) districts.(20)

Preliminary results of a study involving 2069 oil shale workers who had been in the industry for 10-20 years and had been followed for 20 years failed to show an incidence rate for lung and stomach cancer that exceeded that found in the general population. However, the study did reveal an increased incidence of skin cancer among women who had spent between 10 and 20 years in the industry. Purde and Rahu do not distinguish among the several possible job categories involved although it is probable that the population under study excludes miners. Of the 2069 workers studied, 89 individuals with diagnosed cancers were identified. Of these, 23.6% were stomach cancers, 15.7% were skin cancers, 13.5% were lung cancers and 13.5% were tumors of the uterus. Except for uterine tumors these numbers are offered without any distinction between the sexes or any reference to the age of the patients although it must be assumed that most of the population was in or near a general retirement age (55 for women and 65 for men).

The Soviets appear to have put considerable effort into determining the health effects related to oil shale mining. Akkerberg states that the dust concentrations in underground mines ranges from 2 to 30 mg/m³ with a much tighter range in the drifts $(6-9 \text{ mg/m}^3).(21)$ The difference may be related to the process wherein some of the initial crushing procedures and considerable rock dumping take place underground (author, personal observation). Kung cites Feokistor in regard to the relatively fine nature of the mine dust, 80% of which is made up of particles under 2 µm in size. This is a remarkably small, highly respirable dust which, even at low concentrations, might lead to eventual respiratory impairment. Salzman observed signs of pneumoconiosis and fibrotic disease during radiographic examination of workers exposed for many years to mine dust.(22) Kung reported the pathological changes observed during examination of autopsy materials from workers associated with oil shale mining. He states that coniotic fibrosis from long-term inhalation develops slowly and is of a mild, diffuse nature. Much of the inhaled material is transported to the hilar lymph nodes and typical silicotic nodules are found in bronchopulmonary nodes. Significantly, both focal and diffuse emphysema were noted in many specimens and signs of chronic bronchitis were observed.(23) Kung concludes that inhalation of oil shale dust causes chronic bronchitis, mild pneumoconiosis and emphysema, but that the incidence is low. He attributes this relatively low incidence to the low

content of free silica in kukersite and to the low concentration of dust in the mines.

Luts has described the incidence of occupational disease of the nasal portion (including the major sinuses) of the respiratory tract. He reports that 7.2% of the oil shale miners observed suffered from chronic hypertrophic rhinitis often accompanied by sinusitis and nasal polyps. These changes are attributed to the high humidity and cold temperatures (8-9°C) found in the mines and are not considered occupational diseases. Apparently a distinction is made between the "microclimate" of the mines (temperature and humidity) and the concentration of raw shale dust. Contact with oil shale ash (soot), on the other hand, is responsible for a 7.6% incidence of atrophic rhinitis. Luts attributes these more severe changes to the nature of the ash and the additional insult of fugitive gases, an effect he equates to the clinical pattern seen after inhalation of superphosphate or cement. The changes described as related to shale ash are undoubtedly partly due to simultaneous exposure to gases and vapors and points to the need for adequate respiratory protection for U.S. workers who may be associated with working retorts and spent shale as part of their job.(24)

Bogovski described the general problem of occupational skin tumors and suggested several steps to be taken to achieve adequate worker protection and develop epidemiological records.(25) Among measures he listed are: 1) compulsory analysis of occupational and medical histories at frequent intervals; 2) imposition of adequate prophylactic measures and industrial hygiene practices; 3) detection of carcinogenic substances in current and new products; 4) instigation of new experiments to identify the carcinogenic potential of industrial products; and 5) detailed evaluations of the state of health of significant blocs of workers in several production plants.

In summary, several conclusions may be drawn from Soviet reports on human health effects:

- 1. The incidence of stomach and lung cancer is higher in the general population of the oil shale districts.
- 2. This higher incidence is, at least partly, attributed to the immigration of workers from Republics where the background incidence is higher.

- 3. The higher incidence of stomach cancer in rural populations of the same region is unexplained, but does not appear to be associated with elevated levels of BaP in the environment (i.e. soil, water, vegetables, etc.).
- 4. An increased incidence of skin cancer has been observed among female workers.
- 5. Mine dust concentrations are low, much of the dust is highly respirable and the percentage of free silica is low.
- 6. Chronic bronchitis, mild forms of pneumoconiosis and emphysema are observed in miners.
- 7. Diseases of the mucous membranes of the nasopharynx as a result of exposure to raw shale dusts and to a mixture of shale ash and gases/vapors are observed.

OIL SHALE-RELATED HEALTH EFFECTS OBSERVED IN GREAT BRITAIN

History

The Scottish oil shale industry and the English textile industry, which used products derived from shale oil, provided much early information regarding shale oil-related diseases of the skin. Scrotal cancer among Scotch retort men, English "mule spinners" and skin tumors among Scotch paraffin workers were among the first occupational diseases for which compensation was provided.

Occupational Diseases (Great Britain)

An early and thorough investigation of occupational disease was the study of paraffin workers and oil workers associated with the Scottish oil shale industry performed by Alexander Scott in 1923.(26) Scott described, in great detail, the various manifestations of skin disease found in oil shale workers and discussed the etiology, anatomical location of lesions and pathology and suggested prophylactic measures. Seven distinct occupational dermatoses were described: 1) Occupational comedones (acne), 2) Folliculitis and follicular dermatitis, 3) Pustular dermatitis, 4) Papular dermatitis, 5) Erythema simplex 6) Dermatitis erythematosa, and 7) Epithelioma (Paraffin Workers Cancer). Of these papular dermatitis and follicular dermatitis (destruction of hair follicles) were the most common and epithelioma was the most important because of the life-threatening potential.

In 1922 Scott described occupational cancer among Scottish oil workers and stated that the incidence was approximately 1.5% over a 22 year period.(27) This incidence rate is given as a percent of workers observed without a description of the total industrial population or calculation of the years of exposure although a selected group of workers had a minimum of 18 years of service. Scott pointed out three important factors in the occurrence of occupational cancer among shale workers: 1) age at first observation, 2) length of service and 3) influence of job assignment upon location of lesion. From his observations it is apparent that most skin cancers occurred in workers over 40 years of age with more than 18 years of service. The influence of work assignment on anatomical location of the lesion is illustrated by his data which show a predominence of arm, hand,

head and neck neoplasms among paraffin shed workers compared to a high incidence of scrotal cancers among oil workers, retort men and still workers. Scott concluded that direct contact with paraffin was largely restricted to the upper parts of the body while contact with the ash, coke and other "gritty material" experienced by the oil workers was less restricted. He considered that difficulty with, or lack of, personal hygiene was an important factor in the high incidence of scrotal cancer. While paraffin workers cancer was recognized as an occupational disease by the British Workmens Compensation Act of 1906, the Scottish oil shale workers were not officially included until 1920.

Scott described the neoplastic conditions he observed as epitheliomata, and included both benign and malignant tumors. The fatal cases in this series were apparently due to local invasion rather than distant metastases although the investigative techniques of the day may have precluded precise diagnosis.

In 1922, Southam and Wilson described the prevalence of scrotal cancer among "mule spinners" in the British textile industry. The lubricating oils used were of the "paraffin series", were largely shale oil derived and saturated the clothing of the inquinal region of the workers.(28)

In 1926, White discussed occupational dermatoses and stated that the [natural] "petroleums do not usually inaugurate neoplasms" but that in oil shale workers the prospect of developing cancer is 0.5%.(29)

Experimental Results (Great Britain)

Twort and Twort designed skin painting studies in mice to test the relative carcinogenic potency of several oils and developed an arbitrary scale based on their experiments.(30) They ranked shale oil (Scottish) as having a potency of 48 compared to Pennsylvania crude petroleum with a potency of 1 and California petroleum with a potency of 3. Some coal derived materials were considerably higher than shale oil. In a later experiment they showed the process temperature dependency of carcinogenic potential.(31) Leitch also described positive skin-painting experiments with certain fractions of Scotch shale oils.(32)

In 1943, Barenblum and Schoental suggested that the carcinogenic constituents of shale oil were similar to those found in coal tar and that although blue shale oil contained 3:4 benzpyrene some fractions apparently

devoid of benzpyrene induced skin tumors in mice.(33) In 1944, they compared a chloroform extract of finely ground raw shale with shale oil in a mouse skin painting scheme. While they could induce no tumors with the raw shale extract, they caused a 60% tumor incidence in 18 weeks and a latency to first tumor of only 7 weeks with shale oil.(34)

Summary

In summary, several observations can be made from the British experience with oil shale-related occupational disease:

- 1) Most of the occupational diseases identified as being associated with the oil shale industry were the result of skin exposure.
- 2) Length of exposure and age of the worker are important factors in industrially related skin cancers.
- 3) Adequate protective measures, routine in modern industry, could have greatly reduced the risk of occupational cancer.
- 4) Process temperature was identified as a contributing factor to the relative carcinogeneoity of products.

CONCLUSIONS DRAWN FROM FOREIGN EXPERIENCE

Oil shale industries producing a variety of products have existed in both the United Kingdom and the Soviet Union for periods exceeding 50 years. During the years of active production (and continuing in the U.S.S.R.) a substantial body of information involving both experimental data and occupational disease incidence has been developed. From this body of data several conclusions can be drawn as follows:

- Most occupational diseases affected the skin.
 - Observed skin diseases included contact dermatoses as well as benign and malignant neoplasms.
 - Age and length of service were important factors in the incidence of skin cancers.
 - Sound industrial and personal hygiene practices could have prevented or greatly diminished occupational disease.
- Neoplasia, in organ systems other than the skin, has not been frequently reported as an occupational disease.
 - The incidence of stomach and lung cancer is higher in the oil shale producing areas of the Estonian SSR, but this fact may be, at least partly, due to migration from other districts.
- Non-neoplastic lung diseases are not a serious problem in oil shale miners and other workers in the Soviet industry.
 - Chronic bronchitis, mild forms of pneumoconiosis(silicosis) and emphysema are observed.
 - Diseases of the nasopharnyx occur in more severe forms in workers exposed to combinations of ash and gas/vapor effluents.
- A mature shale oil industry is a relatively recent development in the Soviet Union with current technologies existing since 1960 or after. Observation times may be too short for definitive epidemiological conclusions.
- Experimental data from the U.S.S.R. indicate that both direct toxicity and carcinogenicity may be process related.

- Direct (systemic) toxicity is more pronounced with higher process temperatures.
- Direct toxicity may increase as phenol content increases.
- Carcinogenicity of products is related to higher process temperatures.
- The presence of BaP is not a reliable indicator of carcinogenic potential.
- Oil shale dusts have not been shown to be carcinogenic per se.

A mature oil shale industry, located in the intermountain region of Colorado, Utah, and Wyoming will probably consist of a mix of extraction technologies chosen partly on the basis of local geology. Certain health hazards, both occupational and public, can be predicted in a generic sense; however, technology-specific information is crucial to an understanding of the eventual hazards of a truly scaled-up industry. Basically, the technologies can be divided into three major categories: surface retorting (with mining and crushing); modified <u>in situ</u> retorting (with mining but no crushing step); true <u>in situ</u> (with rubbling from the surface and no mining). Each of these categories present certain unique hazard potentials with even more technology-specific questions arising within the surface retorting category.

In addition to the potential hazards of a large regional extraction industry, consideration must be given to the further processing and eventual public use of the refined products. Health and environmental research has therefore begun to address not only the extraction issues but the refining and end-use of the resource. This research extends from site-specific industrial hygiene studies through an array of chemical and biological assays of relevant materials to biological testing of final industrial and consumer products. In some instances workers involved in the oil shale industry have been examined in attempts to either establish the health status of the small population of current workers or to retrospectively determine the existence of specific long-term effects.

The most meaningful way to organize the existing information is to base it on the materials involved rather than on the test systems used. This allows the reader to compare the results of several levels of testing on one class of materials at a time and, in general, to follow the resource from original extraction through end-use. The three major materials categories are: 1) airborne effluents (dusts, vapors, gases); 2) oils and refined products; and 3) Aqueous effluents (retort waters, leachates). Most potential health hazards can be placed in these categories; however, there are certain questions which may be common to all three material categories. Included here is an array of inorganic and organometallic complexes which may be formed and mobilized during extraction and

processing.

AIRBORNE EFFLUENTS

Within the last two or three years, three in situ retorting techniques and one surface retort have been demonstrated at pilot scale. case, field studies with extensive sampling efforts have been conducted to define both the occupational environments and certain more general sitespecific problems. One of the in situ sites utilizes a horizontal burn method in which rubbling is performed from the surface with no true mining. Other than road dust and particulates created during blasting there is very little problem with dusty conditions. The other two modified in situ (MIS) sites depend on considerable underground mining with the attendant problems of dust control. In addition to the particulates associated with nearly continuous mining, the air of large MIS mines may contain fugitive gases/vapors from the burning retorts as well as the ubiquitous diesel exhaust (also a particulate). Surface retorting requires mining (usually room and pillar) crushing and stockpiling of ore before retorting. A commercial-sized surface retort may consume as much as 100,000 tons of shale ore in one day and produce a like amount of spent shale (equivalency in weight is not exact but volume is often increased). Surface techniques, therefore, have the additional problem of large volumes of spent material to be disposed of on the surface. Although several surface retorting techniques have been demonstrated, only one, the Paraho process at Anvil Points, Colorado, has been operated to any extent within the last few years. It is from this production run (1977-78) that most of the currently available materials for testing have become available. (35)

PARTICULATES

No threshold limit values (TLV) have been established for either raw or spent shale dusts per se and any current regulations will have to be based on standard formulas for silica-bearing rock.(36) Dust exposure becomes an important concern when the relatively high free silica content of raw and spent shale (8-15 percent) is considered along with the complex organic materials involved. The presence of free-silica, the chemical availability of organics and the particle size (respirability) are the most important factors in establishing the potential hazard of dusts of this type. Both

raw and spent shale dusts have been analyzed for the availability of total hydrocarbons and certain polycyclic aromatic hydrocarbons as a function of particle size. It was found that chemical availability (and presumed bioavailability) of total hydrocarbons rose as particle size went down.(37, 38)

Long-term studies of rodents exposed to respirable oil shale particulates have failed to produce pulmonary cancers. (38,39,40). These same studies do, however, indicate a potential risk from pulmonary fibrosis and obstructive lung disease which is similar to that associated with other hard-rock mining endeavors. The number of pulmonary experiments is so-far too meager to establish a dose-response or to identify pathological changes representing a specific shale miner's pneumoconiosis.

Small groups of oil shale workers, employed during the infrequent activities at Anvil Points, Colorado, have been examined for pulmonary pathology with inconclusive results. In one report, oil shale pneumoconiosis (or shalosis, the authors' term) could not be confirmed because of the complicated work and smoking histories of the subjects. (41) Another study, which examined workers during the 1977-78 Paraho production run, revealed pulmonary changes with a strong correlation to smoking, but no relationship to oil shale work history. (42) Both studies involved only small populations that worked at the same site during different periods of production activity.

Industrial hygiene surveys and sampling activities have been performed at most of the recently active sites. These field studies include the previously mentioned Paraho run, the Occidental development at Logan Wash, Colorado, the Rio Blanco development on Colorado's C-a tract and the Geokinetics operation near Vernal, Utah. Measurements of dust levels at each site have varied enormously and reflect the experimental nature of some operations and illustrate the operational specificity of particulate contamination. In both MIS operations the measured in-mine dust levels averaged far below an assumed TLV of 2.5 mg/m³ (based on 10% quartz content). Dust levels associated with surface retorting were much more operation-dependent and the highest levels were noted in areas where machinery was remotely operated. In areas around the retort with intermittent worker activity the dust levels were low (generally less than 1 mg/m³ of respirable particulate. However, some remotely operated activities

generated several hundred mg/m³ of total dust at times. In either case the occupational hazard is low; however, based on these findings, controls will have to be imposed on a scaled-up industry to prevent regional problems. There was a somewhat higher dust level in the mine serving the surface retort than in the two MIS mines.(43,44,45) Actual mining conditions could not be compared between MIS and the surface procedures since sampling was not conducted under similar operational circumstances. Gas and Vapor concentrations of selected organic compounds have been measured in both types of extraction procedures, and levels detected were generally below established TLVs. Samples included CO, CO₂, NO₂, NH₃, H₂S, SO₂, CS₂, HCN HCHO, HNO₃, arsine, benzene, toluene, phenols, aliphatic amines and total hydrocarbons. Once again, detectable levels were operation-specific and multiple factors contributed to local work environments (i.e., diesel equipment, blasting, retorting, etc.)

Analysis of fugitive emissions will be a continuing and site-specific need as the technologies develop since each extraction technique and each mine will vary considerably in specific ways. The problems of respiratory or skin contact with organic vapors/gases by themselves or in combination with particulates have not been adequately studied. These are important generic questions which cannot be answered by the usual combination of field study and laboratory experimentation. In both surface retorting techniques and in situ approaches there is a possibility of exposures which combine particulates and organic vapors. For instance, a 50,000 bbl/day MIS facility would require a minimum of 25 large in-place retorts at various stages of retorting to be combined with an equal number of retorts being prepared in adjacent mine complexes. Retort integrity and ventilation will need to be nearly fail-safe to control potential worker exposures. Fugitive vapors and gases may also combine with both raw and spent shale particulates in connection with surface retorts. The only active true in situ operation presents some specific problems. Because the shale has a minor overburden in this formation, blasting to create uniform rubble is performed from the surface with no mining. Creation of a sufficient void volume depends on surface up-lift, which also creates surface cracks. Crack sealing is performed with varying success with the result that gases/vapors can escape during the retort "burn". A similar

situation has occurred twice in recent years when raw shale storage or fine piles have been ignited accidentally. This phenomenon could impact both industrial and regional populations if similar incidents are frequent. Measurements of selected compounds have been made during one recent fire of this type. Measurements taken at fissure openings indicated CO and $\rm SO_2$ levels as high as 1000 ppm, $\rm H_2S$ as high as 500 ppm and total hydrocarbons up to 1000 ppm. However, concentrations detected at an approximate breathing zone (5-6 feet) were within safe limits, indicating rapid dispersal of the emissions. Combustible gases as high as 20% of the lower explosive limit (LEL) were detected at ground level but were also quickly dispersed.(45)

Long- and short-term animal studies addressing these complicated, mixed exposure conditions are only beginning.(46) Both acute and chronic toxicity must be considered if an adequate definition of hazard is to be developed.

PRODUCT OILS AND REFINED FUELS

Nearly all fossil derived liquids can be shown to be carcinogenic. Because of historical evidence, the question of carcinogenicity in connection with product oils and their refined daughter products has become one of the central health concerns associated with shale oil extraction. Standardized up-grading procedures practiced to simplify transportation and refining may significantly reduce the carcinogenic potential of the oils, and modern refinery techniques should minimize occupational exposure. Even with the assumption of modern protective practices, several questions remain, i.e., the relationship of carcinogenic potency and process chemistry, the comparative tumorigenicity of synfuel products in general and with natural petroleums, identification of the factors involved in the apparent reduction of carcinogenicity by hydrotreatment, and a comparison of the inflammatory potential of the crude products and by-products. Ultimately, the products reaching individual consumers or employed as chemical feedstocks must also be measured for toxic and carcinogenic potential.

Because shale oil, along with other fossil liquids, is a highly complex mixture, the results of many of the shorter term assays for mutagenesis

(and mutative carcinogenesis) have been equivocal. Reliance on such tests for definitive risk data is inappropriate and obscures their great usefulness as first-step screens and for indicating trends. Careful studies combining chemical analysis and fractionation with mutagenesis assays can help to identify the active components in fossil fuels and define the generic and process factors which contribute to activity.

Crude oils from most of the recent retorting operations have been tested for mutagenicity using several methods but, principally, the Salmonella/mammalian microsome assay of Ames. (47) While a number of bacterial strains have been used, most of the results are based on histidine reversion phenomena in either TA98 or TA100 test strains of Salmonella. Testing has been carried out both with and without the addition of rat liver homogenate (S9-metabolic activation). Considerable interference by cytotoxicity has been experienced when testing most of the shale derived fuels. This reaction appears to be somewhat process-specific and is more pronounced in the only hydrotreated product tested to date. (48) Cytotoxicity may have some relationship to the inflammatory properties observed after repeated skin application (see below). Because of unequal cytotoxicities, it is sometimes hard to compare the results of oils from different processes. An added complication is the variation in amount of hydrocarbons extracted in the medium-compatible solvent (usually dimethylsulfoxide). Based on research performed so far, the much-tested Paraho crude oil has been shown to be mutagenic for TA98 with S9 activation although the results with TA100 have varied from no activity to quite high revertant frequencies.(48,49,50) There is general agreement that the hydrotreating of this highly active oil reduces the mutagenicity anywhere from three- to Mutagenic activity has been further defined by testing major fractions of the oils, and it has been shown that most of the activity lies in the basic and neutral fractions as derived in the most common separation techniques.(50,51) Experiments utilizing mammalian cell systems to identify mutagenic activity in the various oils have been performed both with and without exogenous metabolic activation. The cellular toxicity of the highly complex mixtures again interferes with straightforward analysis of mutagenic activity. (52) The mutagenic enhancing properties of nearultraviolet (NUV) have been studied with both the crude oils and certain process waters. (53) While photo-induced mutagenicity was reduced by hydrotreating,

phototoxicity was not affected. This observation may be important in considering industrial situations where exposure to sunlight and crude oils may be difficult to prevent.

Cytogenetic studies, in which structural changes in chromosomes or actual aberrations are observed, have been performed with several oils (49,54,55). The cytogenetic assay measuring sister-chromatid exchange (SCE) can be performed both in vitro and in vivo. Timourian (49) found no increase in SCE in mice treated with either crude or hydrotreated shale oil until doses approaching the mean lethal dose (LD₅₀) were used, while others using a cultured mammalian cell (CHO) observed a significant dose-related SCE induction with crude oil. Response to hydrotreated crude oil was of less magnitude; however, normalization of the data according to the amount of extractable material (DMSO extraction) revealed an SCE induction rate nearly equal to that of the parent crude. When actual chromosome breaks were measured after exposure of mice to crude shale oils or hydrotreated crudes, the frequency of aberrations observed with oils from different processes were about the same while the upgraded oil showed a similar trend but a lower frequency rate. (55)

Intact animal testing, focused mainly on skin cancer potential, has been performed by a number of investigators. The principal method used has been the repetitive direct application of materials to mouse skin. (56) All of the crude shale oils tested in recent experiments have exhibited a carcinogenic effect in the mouse system. (57,58,59,60) Certain of these experiments have also demonstrated the carcinogenic potential of coalderived liquids, natural petroleums and up-graded (hydrotreated) shale oils as well as certain shale-derived refinery products. From this accumulated body of work several preliminary conclusions or trends can be identified: 1) carcinogenic potential is common to most fossil liquids; 2) crude shale oils appear to be more carcinogenic than most natural petroleums; 3) hydrotreating reduces carcinogenic potential markedly; 4) among shale oils, potency may be process specific; 5) coal derived liquids equal or exceed the potency of shale oils; 6) none of the distillates have been shown to induce skin tumors in the mouse system. Along with tumor occurrence and latency, the phlogistic or irritant properties of the oils have been demonstrated. Various forms of acute and chronic dermatitis (non-neoplastic) may be at least as important as occupational diseases as is skin cancer. The irritant properties of shale oils have been demonstrated in several of the same studies that have identified the tumorigenic potential. It has been shown that, within certain limits, frequency of exposure is the major factor in severe inflammation. Frequency of exposure also has a noticeable effect on tumor latency. Sustained heavy and frequent exposure of mice cannot be considered analogous to industrial exposure, but the observations, nevertheless, illustrate several important points: 1) occasional exposures, even if heavy, will probably not lead to a long-term effect; 2) sustained intermittent exposures may eventually lead to neoplasia but the latency (time to tumor occurrence) is probably lengthened as the frequency of exposure is diminished; 3) inflammatory phenomena are usually related to frequent, repeated exposures.

Observations on the cutaneous effects of shale oil in humans have been reported in nearly every country where an industry has existed. (See section on Foreign Experience with Oil Shale Production). Limited studies on U. S. oil shale workers have been performed, and no relationship could be found between the observed skin lesions and the degree of exposure to shale oil. The contributing factors of age, complexion, sun exposure and other occupational variables complicate any retrospective studies of skin disease. To date the U. S. populations have been too small for adequate analysis.(61)

Systemic toxicity resulting from cutaneous exposure must also be considered with materials of this nature. An apparent nephrotoxicity in mice has been reported following sustained high-dose skin applications of certain distilled refinery products. (62) Similar kidney lesions have been observed in male rats following oral exposure to naval jet fuel derived from either shale oil or natural petroleums. (63) It should be borne in mind that skin exposure in animals can lead to oral exposure (because of self-grooming) and that systemic effects may therefore be the result of more than one exposure route.

WATERS

One of the least understood health implications of a producing oil shale industry is the possible effect on the waters of the region. Water contamination is possible in a variety of ways but because of the uncertainties as to the number of extraction facilities to be built and

what processes will be involved, it is difficult to predict contamination scenarios with accuracy. The question is further complicated by an incomplete understanding of the temporal aspects of aquifer contamination, (i.e. when MIS retorts will be allowed to reflood, the rate at which contaminants are transported, etc.).

Contamination can come from two principal sources: 1) as a product of the retorting process (so-called process or retort waters) and 2) contact between retorted shale and "natural" waters (leaching of spent shale piles or reflooding of burned out retorts). In addition, there is the possibility that retort process waters, which may amount to as much as three barrels of water for every gallon of oil produced, may be used in dust abatement procedures. Under certain circumstances this could have a compounding effect by causing leaching of spent shale with already contaminated water. It is likely, however, that most process waters from above-ground retorts will be impounded and subjected to clean-up techniques before disposal or industrial use within the plant itself.

Positive mutagenicity in the Ames assay has been shown in one above-ground retort process water. (64) This water would be industrially described as "tank bottoms" and represents a worst case situation which would nonetheless have to be addressed in designing clean-up techniques. The organic compounds or compound classes that are responsible for this activity have yet to be determined. The same water has been shown to contain direct-acting mutagens in assays using mammalian cells (no metabolic activation required).(65) Prenatal toxicity studies in breeding mice were also performed on this water and demonstrated no differences in number of pregnancies, maternal weights, number of live fetuses or average fetal weight. There was, however, an apparently dose-related abnormality of the hard palate and some indication of an increase in preimplantation fetal loss. When the experiments were repeated with the same process waters after about six months of cold storage, fewer significant abnormalities were observed. (66) One possible explanation is that the biological activity was reduced with time, a conclusion which would seem to indicate that standard clean-up techniques such as filtration and impoundment can be useful.

Product waters from two in situ processes have been assayed for mutagenic activity by several investigators. Waters from an MIS retort were

found to be negative in the Ames assay while process waters from a true in <u>situ</u> retort were marginally positive.(64) When these same waters and the above-ground process water were screened for <u>in vitro</u> induction of sister chromatid exchange, only the surface process water was found to be positive.(67) Earlier investigators had found the MIS process water to be marginally positive for mutagenesis in the Ames assay.(68)

Some attempts at comprehensive chemical analysis of these waters have been made, and tentative results indicate that the above-ground retort water is higher in carboxylic acids, amides and nitrites. (69) More effort should be expended in chemical analyses of retort waters and the relationship of their chemical make up to the product oil established on a process specific basis if predictions of necessary control procedures are to be made. important question of spent shale leaching either in MIS retort-abandonment procedures or in surface disposal techniques has only begun to be addressed. Several investigators have identified the potential for mobilization of several environmentally important and potentially toxic trace elements. Included here are boron, fluorine, molybdenum, arsenic, selenium, vanadium, nickel and mercury. Under retorting conditions, there is also the potential for formation of such materials as nickel arsenides. (70,71)The temperatures at which nickel, sulfur and arsenic compounds are known to form are comparable with those seen in most retorting processes. (72) Unfortunately, some of the metallic compounds that have been shown to be carcinogenic are refractory to testing by standard mutagenesis assays.(73)

Aqueous materials somewhat analogous to <u>in situ</u> leachates but referred to as a retort water have been subjected to toxicity testing by several methods. (74) These studies which included direct toxicity testing in laboratory animals and tests for teratogenesis revealed a low toxicity and no apparent fetal toxicity. These so called retort (or process) waters were highly diluted by infiltrating ground waters and may represent the "best" case situation. With intense development of large <u>in situ</u> facilities, the positive dilution factor may be appreciably diminished in contiquous aquifers.

The potential of water contamination remains the most complex and most ill-defined health-related issue associated with oil shale extraction. Water contamination, if it occurs on any scale, may also have an important impact on public health in the region; an impact that is perhaps as

important and probably more insidious than reductions in air quality. It will take comprehensive studies combining geochemistry, hydrology, analytical chemistry, and biological assays on both a generic and site-specific basis to determine the potential hazards.

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SUMMARY AND CONCLUSIONS

While similarities between the health impacts of oil shale development in various countries exist, there are crucial differences that preclude making judgments on the potential effects of a highly developed U.S. industry. Current research, focused on American materials and technology, has begun to identify specific concerns which will be germane to oil shale development in the United States. From a study of both the historical evidence and the results of current research, several observations can be made;

- 1) The major current health concerns relate more to occupational rather than regional health hazards; however, as the industry scales up, such problems as raw shale ignition, aquifer contamination, and leaching of spent shale from surface disposal may affect regional populations.
- 2) Neither the historical evidence from other countries nor the results of current research have shown pulmonary neoplasia to be a major concern. Surveillance for non-neoplastic pulmonary disease should be continued both experimentally and epidemiologically since U.S. materials are much higher in fibrogenic compounds (silica).
- 3) Exposures from mixed sources, especially particulates in combination with organic vapors have not been adequately studied and risk cannot be predicted until meaningful experiments have been accomplished.
- 4) Skin disease, including neoplasia and benign dermatoses, may be a problem in the industrial populations; however, modern protective practices and production techniques will reduce contact. Upgrading of crude oils by hydrotreatment serves to reduce but not eliminate the carcinogenic potency of the crude oils.
- 5) The question of regional water contamination and any associated health hazard has not been adequately addressed. Meager current data coupled with a lack of information on which technologies will succeed and on what scale make useful extrapolations difficult to develop.

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