A PETROLEUM INDUSTRY PROGRAM TO EVALUATE THE HEALTH RISKS OF OIL SHALE MATERIALS AND OPERATIONS

R. L. Gibson, M.D.
Gulf Science & Technology Company
P. O. Box 2227
Houston, TX 77001

N. K. Weaver, M.D.
American Petroleum Institute
2101 L Street, N.W.
Washington, D.C. 20037

ABSTRACT

Health risks of shale operations are documented in the literature. Benign and malignant skin conditions were reported in Scottish workers who processed shale and in English cotton mule spinners who used shale oils in the nineteenth and early twentieth centuries. More recently carcinogenic fractions of oil shale materials have been identified.

The American Petroleum Institute is sponsoring an extensive research program to evaluate the health risks of oil shale materials and operations. Comprehensive toxicological studies are underway while industrial hygiene and epidemiological investigations are being planned. The objectives, development and status of this research program are reviewed.

INTRODUCTION

The American Petroleum Institute (API) is a trade association representing 350 companies in the petroleum industry. For more than ten years, health-related research has been conducted by the API on a wide variety of generic products and in the areas of occupational and environmental health and industrial hygiene. The cost benefits of this program to the industry are obvious: duplication of studies is avoided; there is better use of limited scientific resources; and the petroleum companies can focus their research on proprietary materials or other occupational health projects. The principal objective of the research program is to prevent disease and maintain health by characterizing the health risk, if any, of the materials which are tested. Employees, customers, consumers, and the general public all benefit.

Medicine and Biologic Science Division, API

In the API organization, the Medicine and Biologic Science Division is responsible for initiating, planning, monitoring, and auditing these research projects. There is a pooling of talent including physicians, industrial hygiene engineers, toxicologists, analytical chemists, and scientists in other disciplines. The ability to call on the collective judgment of these scientists with many years of training and experience in the industry to establish research priorities and manage projects benefits all parties and strengthens the research effort.

Task Force Established

Because many member companies in the API were interested in shale technology, the Medicine and Biologic Science Division established a multidisciplined task force in 1974 to determine the health-related research needs in the shale industry. The pertinent literature was reviewed and the historical highlights are of importance in understanding the occupational health concerns and needs for research in the industry today.

Literature Reviewed

The hazards of mining operations are well documented. In 1713, Bernadino Ramazzini, father of occupational medicine, said: "So many and so inexplicable are the

mixtures of metals in the bowels of the earth that it is almost impossible to determine precisely what injurious element is present in this or that mine." Coal workers' pneumonoconiosis and silicosis are examples of risks that still are encountered in underground mining.

In 1775, Percival Pott in England recorded the first occupational cancers in chimney sweeps. Many English sweeps developed scrotal cancers. English sweeps seldom bathed, while German sweeps who washed daily and Scottish sweeps who used cleaning brooms did not develop such cancers.

In 1876, Joseph Bell reported two cases of paraffin epithelioma of the scrotum in laborers in a shale oil works in Scotland. In a paper published in 1923, Alexander Scott reviewed reports of skin and scrotal cancers in Scottish shale oil workers. In his capacity as medical examiner for Scottish Oils Limited, he performed periodic examinations on 200 workers in the paraffin departments. He found a variety of benign skin lesions, such as comedones, warts, papules, folliculitis and pustules, occurring in approximately fifty percent of these men. Nineteen cases of skin cancer were reported over a 22-year period. During the same period, 46 skin cancers were seen in a group of 5,000 workers in the industry, including retortmen, oil refiners, stillmen and laborers. Skin cancers of paraffin workers usually arose from warts or papules on the hands and forearms while scrotal cancers were more common in the larger workforce.

The final scene in this Scottish tragedy was played by the mule spinners in the cotton textile industry in Britain. Mule spinners' cancer was seen with increasing frequency from the mid-nineteenth to the mid-twentieth century. From 1911 to 1938, more than 500 deaths from scrotal cancer were reported in cotton mulespinners. Mule Spinning Special Regulations, adopted in 1953, required that process oils used in the industry be of animal or vegetable origin or drastically refined mineral oils. The incidence of cancer was dramatically reduced.

Other human studies of Estonian oil shale workers confirmed the potential toxicity of oil shale materials, particularly skin and lung conditions, but cases of occupational cancer were not reported (Bogovsky and Janes 1975). Studies in the 1950's revealed a high incidence of benign skin lesions in workers at the Oil Shale Demonstration Plant of the Bureau of Mines near Rifle, Colorado (Schwartz and others 1957).

Published data on the toxicity of oil shale materials in animals have emphasized the carcinogenic potential. Leitch (1922) first demonstrated the carcinogenicity of Scottish shale oil in mice. Warts and skin cancers were produced by all of the fractions tested; experimental results appeared to confirm the clinical observations of workers. In 1943, Berenblum also produced tumors in animals exposed to shale oil. Smith and others (1951) reported that whole shale and fractions above 700°F did not show carcinogenicity in mice, but the middle fraction, 550-700°F, and the combined fractions showed mild carcinogenicity. Heuper (1957) produced skin cancers in mice exposed to shale oil by skin painting and by subcutaneous injection.

Animal studies of the toxic properties of Estonian shale process materials were conducted by the Estonian Institute of Experimental and Clinical Medicine. Inhalation studies in rats of mixed dust encountered in the oil shale industry did not produce a significant fibrosis. Intratracheal introduction of shale oil coke in rats produced a moderate proliferation of interstitial tissue during eight months of exposure. Shale oils were reported to exert a gonadotropic action in rat experiments. Carcinogenicity studies in mice showed a strong carcinogenic action of the high temperature (chamber oven) oil. Intermediate fractions produced moderate carcinogenic activity. Water-soluble phenols from shale oils were shown to have a promoting action on benz-a-pyrene carcinogenesis in mice (Bogovsky and Janes 1975).

Table 1. API shale toxicity testing program.

MATERIAL	LOCATION	PROCESS	Acute	Carcinogenesis	Chronic Inhalation	Mutagenesis	Teratogenesis	Analytical
Raw Shale	Anvil Points		x	x	x	x	x	x
Raw Shale	Ca Tract		x	x				x
Raw Shale	White River		x	x				x
Shale Oil	Parachute Creek	Tosco	x	x		x	x	x
Shale Oil	Anvil Points	Paraho(D)[1]	x	x		x	x	x
Shale Oil	Anvil Points	Paraho(D)[2]	x	x				x
Shale Oil	Parachute Creek	Union B	x	x		x	x	x
Spent Shale	Parachute Creek	Tosco	x	x				x
Spent Shale	Anvil Points	Paraho(D)[1]	x	x	x	x	x	x
Spent Shale	Anvil Points	Union B	x	x				x
Spent Shale	Parachute Creek	Union SGR	x	x				x

(1) Direct-fired (2) Indirect-fired

in monkeys and terminal gross and microscopic pathology. Exposure began in April 1977 and, since the study is incomplete, status report cannot be made now.

Genetic Mutations - The genetic properties of one raw shale, three shale oils, and one spent shale were evaluated in a battery of tests consisting of gene mutation tests in bacteria (Ames test), a test for mitotic gene conversion in yeasts, gene mutation tests in culture mammalian cells and in vivo chromosome analysis in rat bone-marrow cells. This series of tests provides a sensitive screen for the detection of substances which produce mutagenic alterations. Positive tests are an indication that the test substance has mutagenic activity and may indicate carcinogenic potential. Negative tests suggest that the test substance lacks genetic activity, but are not

Atwood (1974) reported the results of a lifetime skin painting study in mice. Raw shale oil produced by the Tosco II process and hydrotreated shale oil were tested along with several petroleum products. It was tentatively concluded that the carcinogenic potential of whole shale oil was similar to that of many petroleum products and that upgraded shale oil was substantially less carcinogenic.

Shale Oil Processes Hazards Incomplete - The literature review revealed that knowledge of the health risks associated with the new shale processes and their variety of intermediates and products was incomplete. The API task force designed toxicological protocols to fill the gaps and define the toxic properties of selected materials. A three year program was recommended and funded in late 1975. In December 1975, a seminar was held in Chicago with representatives of the oil shale industry to discuss the health implications of oil shale operations and both medical and technical papers were presented. Meetings were also held with representatives of ERDA to review the research program.

Benchmark Toxicological Standards Established

In 1976, the analytical committee of the Medicine and Biologic Science Division reviewed the available analytical data on shale materials and concluded that benchmark toxicological studies should involve the testing of more than one sample of raw shale, retort oil, and spent shale. This recommendation was based on the technical literature and data submitted by several member companies which indicated significant differences in the composition of materials that might influence their toxicity, including carcinogenicity.

Studies have shown that the composition of raw shale and its organic matter vary with the depth of burial. Concentrations of minerals and trace elements in raw shales also differ considerably. In addition to raw material variability, the type of retort process was found to have significant effect on the nature of recovered oil and spent shale. Consequently, eleven materials, representative of various geographical locations and retorting processes, were selected for extensive toxicological evaluation. Table 1 lists these materials, their geographic sites of origin, the process and the recommended toxicity studies. This extensive program was designed to assess the nature of the exposure, as related to the workplace, and to evaluate the suspected health risks associated with these operations.

Health Risks from Eleven Shale Materials

Short-term studies were done on all eleven materials. Standard protocols were followed to determine the oral LD_{50} in rats, skin and eye irritation in rabbits, skin absorption in rabbits, and skin sensitization in guinea pigs. These studies are complete; the results are being reviewed by the task force and will soon be available.

Skin Cancer - Carcinogenic potential of all eleven shale materials is being evaluated by applications of each material to the skin of 50 mice twice weekly for 18 months or, until gross diagnosis of a carcinoma, followed by lifetime observation. This study, begun in July 1977, followed a pilot study to determine dosage and method of material application. Although the study is incomplete, a preliminary report was made in February 1978 to the Environmental Protection Agency, under Section 8(e) of the Toxic Substances Control Act, advising that benign and malignant tumors have developed on the skin of mice repeatedly painted with the raw shale oils.

Inhalation Dangers - A chronic inhalation study was designed to determine the toxicity of shale materials by exposing experimental animals under appropriate laboratory conditions. Groups of rats and monkeys, equally divided as to sex, are being exposed to a low and a high concentration of raw shale and a spent shale dust for 6 hours per day, 5 days per week, for two years. Response criteria will include observations of body weight, hematologic and biochemical variables, pulmonary function

sufficient for an unequivocal determination of genetic safety since these tests are relatively new and currently being evaluated. These mutagenic studies on the shale materials are complete and are being reviewed by the task force.

The shale materials tested for mutagenicity are also being investigated for teratogenicity by exposing pregnant female rats to graded airborne concentrations of the test materials on days 6 through 15 of gestation. On day 20 of gestation, the rats are sacrificed and the uterine contents examined for the number of live and dead fetuses and implantation and resorption sites. A status report cannot be made since these studies are incomplete.

Analytical Program Objective

The objective of the analytical program is to characterize all samples of raw and spent shale and shale oils selected for the study. Samples will be analyzed in sufficient detail to document differences in composition due to the sources of the raw material or the nature of the retorting process. Shale analyses will include the determination of the major mineral species, Fischer Assay, particle size distribution and a determination of the concentration of benzene extractables, trace metals, and selected radionuclides. Analyses of retort oils will include measurements of critical physical properties; determination of gross hydrocarbon composition; and analyses for selected trace elements and individual polynuclear aromatic hydrocarbons. These studies have been completed recently and are being reviewed by the Analytical Committee.

The information from these toxicological and analytical studies is considered essential in establishing safe exposure levels and in determining appropriate medical and industrial hygiene surveillance procedures. It will also be helpful in developing training programs for workers.

Proposed Occupational Health Studies

A protocol has been prepared by the Los Alamos Research Laboratory and industry scientists for occupational health studies to be conducted at the Paraho oil shale site under joint API and Department of Energy (DOE) sponsorship. The proposed occupational health studies will include occupational medical studies and field industrial hygiene surveys.

Medical studies will include medical examinations of workers to determine their current health status and to establish a data base for a long-term prospective epidemiological study. Participation will be voluntary. Past and present medical records will be reviewed; a comprehensive medical examination with particular attention to the skin and lungs will be performed. Sputum cytology, cytogenetic studies, a urine Ames test, and other special studies are being considered. Surveillance will be continued on a regular basis and follow-up procedures will be designed to follow potential hazards and effects, as determined by the initial findings.

The industrial hygiene survey will identify and quantify the types of materials and stresses to which workers are potentially exposed at the Paraho plant and integrate these findings with toxicologic and other occupational health data. The study will include all operations: mining, crushing, retorting, spent shale disposal, product handling, and transportation, as well as maintenance, routine and unique operations. Air concentrations of dusts and chemicals will be measured, including physical and analytical evaluations. Noise, heat, and other physical factors will also be studied. Results of these findings will be used to design effective engineering control measures that may be extrapolated to commercial scale plants.

SUMMARY

Since the first description of an occupational cancer from exposure to shale oil in 1876, evidence has been accumulating that shale-derived materials may be toxic and, in particular, carcinogenic. Analytical studies report the presence of polynuclear aromatic hydrocarbons; a significant number are known to be carcinogenic. Laboratory reports of animal and human toxicity confirm potential health risks. While occupational risks associated with the new shale processes are recognized, they are not completely understood. Data from the toxicological studies of shale process materials now being conducted by the API and other investigators around the world are important in establishing safe exposure levels and cost-effective engineering controls. In the meantime, it is necessary to employ conservative measures to eliminate or reduce health risks. An awareness of these risks, coupled with our present capabilities in preventive medicine and in engineering design, should assure a safe and healthful workplace in the research projects of today and the commercial operations of the future.

REFERENCES

Atwood, M. and Coomes, R., 1974, The questions of carcinogenicity in intermediates and products in oil shale operations: The Oil Shale Corporation, Rocky Flats Research Center.

Bell, J., 1876-1877, Edinburgh Med. J., v. v. 21, p. 135.

Berenblum, I. and Schoental, R., 1943, Carcinogenic constituents of shale oil: Brit. Expt. Path., v. 24, p. 232-239.

Bogovsky, P. and Janes, H., 1975, Toxicological and carcinogenicity studies of oil shale dusts and shale oils: Instit. Exper. and Clin. Medic., Estonian, USSR.

Hueper, W. C., 1957, Environmental factors in the production of human cancer: Cancer, Butterworth, London, v. 2, p. 404.

Hueper, W. C., and Cahnmann, H., 1958, Carcinogenic bioassay of benzo(a) pyrene-free fractions of American shale oils: Arch. Path., v. 65, p. 608-614.

Leitch, A., 1922, Paraffin cancer and its experimental production: Brit. Med. J., v. 2, p. 1104-1106.

Mule Spinning (Health) Special Regulations, 1953: S.I. No. 1545, H.M.S.O., London.

Pott, P., 1775, Chirugical observations relative to the cataract, polypus of the nose, the cancer of the scrotum, the different kinds of ruptures and the mortification of the toes and feet: London.

Ramazzini, B., 1713, De Morbis Artificim.

Scott, A., 1923, The occupation dermatoses of the paraffin workers of the Scottish shale oil industry, with a description of the system adopted and the results obtained at the periodic examinations of these workers: Extracted from Eighth Scientific Report, Imperial Cancer Research Fund.

Schwartz, L., Tulipan, L. and Birmingham, D., 1957, Occupational diseases of the skin: Shale Oil, Lea & Febiger.

Smith, W., Sunderland, D. and Sugiura, K., 1951, Symposium on cancer control program for high-boiling catalytically cracked oils: Experimental analysis of the carcinogenic activity of certain petroleum products: Arch. Ind. Hyg., v. 4, p. 299-314.