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I. INTRODUCTION

Health protection concerns (including industrial hygiene, safety, and occupational medicine) must be evaluated to insure that development of the oil shale industry proceeds without significant risk to the health of the workers involved. These concerns need to be identified in the early stages of developing this industry.

To provide a basis for discussing potential health protection concerns related to oil shale, it is necessary to briefly discuss the magnitude and characteristics of this resource; the alternate proposed technologies; and the unit operations which make up the operating system. This subject has been detailed in many publications, among them reports prepared for the Environmental Protection Agency.^{1,2} This discussion will be limited to providing sufficient background to put industrial hygiene and other health protection concerns in perspective, and will include a brief description of typical technologies under consideration. It will not provide a detailed description of these technologies, or attempt to cover all the alternate technologies which may be applied to the development of oil shale. However, a basis for considering potential health protection problems associated with development of this industry will be established.

II. BACKGROUND

Oil shale is one of the largest undeveloped fossil energy resources in the United States. It is estimated that high grade shale (greater than 25 gallons per ton), capable of providing 600 billion barrels of oil, exists in

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Utah, Wyoming, and Colorado. If we assume one hundred percent recovery of the oil from this resource, and our present domestic use rates, this represents on the order of a one hundred year supply. In addition to this high grade resource, there is estimated to be 1,600 billion barrels of oil in lower grade (less than 25 gallons per ton) shale in the continental United States.^{3,4} A resource of this magnitude can be an important factor in alleviating the current energy problems which forces the United States to rely extensively on oil imports.

Current research is directed at development of efficient mining, processing, and refining techniques in an effort to tap this large potential source of oil. During this development period, occupational health studies are necessary to assure that working conditions, and the potential health problems associated with this industry, are properly evaluated to assure adequate health protection for workers in existing and future facilities. Data developed under present operating conditions must be carefully analysed and extrapolated to permit application to large commercial systems planned for the future. These extrapolations, may involve significant uncertainties because of changes between development and commercial scale operations. However, such extrapolations are necessary to assure that commercial facilities incorporate appropriate and adequate control procedures.

"Oil shale is a rock in which the mineral portion is associated with high molecular weight organic material in a complex manner. The mineral portion is primarily a marlstone or mixture of calcium and magnesium carbonates (dolomite) with smaller portions of quartz and silicates. Small amounts of sodium and aluminum materials also occur as pockets in some oil shale deposits. The organic portion is principally a material called kerogen, which is of such high molecular weight that it is not extractable by ordinary aromatic solvents. A second organic constituent is bitumen, which is extractable by benzene and other solvents.⁵"

In order to obtain oil from this material, it is necessary to decompose the kerogen in some manner, and convert it into compounds that can be separated from the mineral matter either by distillation or solvent extraction. Oil retorting processes currently under investigation use heat, usually derived from combustion of a small part of the material used in the process, to achieve this goal.

There are three general methods for commercially extracting oil from shale. These are: in-situ; modified in-situ (MIS); and above ground retorting.

For the in-situ process, separation is obtained by ignition of the material underground using an external source of fuel, and then establishing a continuous process as the kerogen decomposes and the oil and gases are driven off while the remaining carbon in the oil shale burns to sustain the temperature. This requires that the mineral be broken up underground so that air can enter, and the oil can escape and be removed through an opening distant from the flame.

A modification of this process, called the Modified In-Situ process (MIS), first involves the removal of 20 to 40 percent of the mineral by mining. Columns of approximately 100 to 150 feet in diameter, and several hundred feet high, are then rubbleized by explosives to create a matrix with voids sufficient for air and product penetration. This rubbleized column is ignited at the top so that heat pyrolyzes the kerogen to produce a mist which can be collected at the bottom of a column. In order to provide a commercial size facility, on the order of 100 or more rubbleized columns will be operated simultaneously. Since a significant fraction of the mineral is extracted in this process, it is likely that an above ground retort will be operated in conjunction with the MIS process.

The third process, which probably is furthest along the road to commercialization, involves above ground retorting. This requires mining the material in relatively large mines, and handling large quantities of material. For a commercial facility one would expect to handle one to two tons of mined material per barrel of oil produced. This would result in 50,000 to 100,000 tons per day being produced as a solid waste product in a typical commercial size facility. While room and pillar mining appears to be the most likely process, open pit mining may also be employed when geological conditions are appropriate. After mining, the material will be transported to a crusher to size it for retorting in an above ground retort. Waste material will result from the crushing operation (material of inappropriate sizes), and from the retort (spent shale). During the retorting process waste gases and aerosols will be collected separately from the product. The crushing operation may be located remote from, close to, or within the mine area. Retorting may involve combustion within the retort (direct process) or by mixing pre-heated gases or solids with the oil shale (indirect process).

III. INDUSTRIAL HYGIENE CONCERNS

Some of the major industrial hygiene concerns which are associated with operations of this type include the following:

1. Inhalation of dust, gases, and vapors associated with mining.
2. Inhalation of dust, gases, and vapors associated with conveying large quantities of materials from the mine, to the crusher, to the retort, to the waste pile.
3. Inhalation of dust, gases, and vapors resulting from fugitive emissions from the retort or crusher.
4. Inhalation of dust, gases, and vapors resulting from managing the waste pile.

These four concerns may be considered as a single item; that is protecting the worker against inhalation of potentially toxic materials. Based on the materials to be handled, and field studies which have been performed, exposure to silica appears to constitute a significant concern. This is not a new or unique problem, but is one which will require careful attention during development of the industry. In addition, there is concern with exposure to organics, trace metals, oxides of nitrogen, carbon monoxide, SO₂, aldehydes associated with operation of diesel equipment in mining operations, and mixtures of chemicals unique to the oil shale processes.

5. Skin or inhalation exposure to hydrocarbons or metals which may be potential carcinogens.
6. Exposure to materials during routine or atypical operations which can result in dermatitis or skin sensitization.
7. Exposure (inhalation or skin contact) during normally scheduled maintenance operations.
8. Exposure to noise levels associated with some unit operations.
9. Exposure to excessive heat sources associated with some unit operations.
10. Need for respiratory protection for non routine (maintenance) or special operations.

Many of the industrial hygiene concerns previously listed are not unique to the development of oil shale. They have been controlled in the mining, and

chemical industries, and many of these control procedures are currently used to protect oil shale workers. However, the MIS process presents several unique industrial hygiene concerns.

To assure that a scientific basis for developing the necessary controls exists, industry, the American Petroleum Institute, the Department of Energy, the Environmental Protection Agency, and the National Institute for Occupational Safety and Health have invested considerable time, money, and effort into field sampling studies and assessments to develop the necessary data. A review of some of these studies⁵⁻¹² indicate that much information is known about existing or past oil shale operations. In some instances data was primarily designed to evaluate environmental concerns, with industrial hygiene applications being a secondary consideration. However, since workers will constitute the most significant population at risk, it is desirable that future studies focus on evaluating industrial hygiene and safety risks. This focus is necessary since any extrapolation from existing relatively small facilities, to future commercial size systems, is dependent on obtaining data from field studies which can directly relate potential worker exposure to the different unit operations. With this information industrial hygiene concerns in future oil shale facilities, which will be different in type and size, can be designed to adequately control worker exposures. This extrapolation problem is compounded by the fact that existing operations are experimental in nature, and typical operating characteristics are difficult to define.

It must be realized that future critical exposure conditions may be related to present atypical exposure situations rather than "normal" conditions. Data obtained under these atypical situations cannot be ignored.

Previously published studies also suffer from generally being in-house reports (i.e. EPA, DOE, LASL, or Bureau of Mines) which have not undergone the scrutiny of peer review associated with publication in the open literature. It is important that reports summarizing studies in this area be submitted for publication in the open literature.

Some conclusions from the referenced studies include the following:

1. Dust exposure to siliceous materials during mining, crushing, and waste disposal present a potential problem, and will require the application of engineering controls. Even allowable nuisance dust levels are exceeded.

2. Fugitive emissions from above ground retorting operations will require careful attention including maintenance of seals, development of standard operating practices, and availability of appropriate control equipment.
3. Size characterization of airborne dusts show that these materials are within the respirable size range for many operations, and could present an inhalation hazard.
4. Immediately following blasting, gas and vapor levels exceed allowable limits, therefore ventilation and work practices must be incorporated into designs to avoid unacceptable worker exposures. This may be especially critical in the MIS process.
5. The presence of extractable organics suggests the need for worker protective clothing which will limit skin exposure to those materials that may constitute a potential source of skin sensitization, or dermatitis. These materials may also be potential carcinogens.
6. There is a need for total respirator programs to provide worker protection for some activities that are not amenable to engineering or administrative controls.
7. There is a wide variation in the dust, gas, and vapor contaminant levels measured due to the different operations, and changes in the operational characteristics of processes under development. This indicates the need for relating air concentrations of contaminants to operating characteristics of the unit operation.
8. The prevention of occupational traumatic injury is a significant health concern.
9. Medical evaluations of the Parahn workers indicate no health problems or effects associated with these oil shale operations. However, these conclusions are limited by the relatively small number of individuals and few long term exposures represented by these studies, and limited data correlating exposure with the individual worker.

IV. ACTIONS REQUIRED TO ASSURE ADEQUATE CONTROLS

Many of the previously identified concerns are amenable to engineering and administrative controls. The industry is well aware of most of these potential problems and are actively working to implement programs to evaluate and control these problems to assure that workers are adequately protected. Safety, industrial hygiene, and occupational medicine programs have been initiated to develop data to provide an estimate of the potential hazard and to assure that adequate controls are used.

It is important to distinguish between hazard and toxicity when considering necessary control practices. In estimating hazard it is necessary to integrate the toxicity of the material with the potential for worker exposure (in terms of concentration and time) to these materials. Simply focusing on toxicity can lead to mis-direction of available resources.

Most of the concerns previously noted can be controlled with existing technologies involving individually or a combination of:

1. Local exhaust ventilation and air cleaning.
2. Enclosure and confinement of dust sources.
3. Development of detailed industrial hygiene and safety work practice guidelines. These would cover what health protection practices the individual worker must follow, as well as the responsibility of management and supervisory personnel.
4. A training program to make workers aware of potential health and safety hazards, and assure familiarity with appropriate work practices.
5. A management commitment to assure that work practices are followed, and engineering controls are maintained to satisfy the original design criteria, or modification of these design criteria based on new information.
6. The establishment and maintenance of an industrial hygiene sampling program to continually evaluate potential hazards to the worker. This is especially critical because of the changing nature of the operations during the development and initial commercialization phase.

7. Involvement of industrial hygiene and safety personnel in all phases of process development and engineering design to assure that proper consideration is given to engineering controls (local ventilation, noise control etc.), maintenance requirements, atypical operations, and human factors.
8. Establishment of a complete respirator program to assure that use of this control procedure provides the level of protection expected.
9. Establishment of guidelines for the use of protective clothing and good hygienic practice consistent with the potential for skin exposure to toxic materials.
10. Establishment of a hearing conservation program, which will include audiometric testing; guidance for the use of hearing protective equipment; and noise surveys to define potentially hazardous areas.
11. Establishment of an occupational medicine program to monitor workers health.
12. Air sampling at selected work sites to provide input to ongoing toxicology efforts.

These programs will provide a high degree of assurance that workers health will be adequately protected under most circumstances. However, there are some potential problems which cannot be quantified at the present time. These require close monitoring of the workers health (as part of satisfying requirement 11 above), and an investment in applied studies in the lab and field. The three most critical problems falling in this area relate to:

1. Hazards associated with the Modified In-Situ technology which will present problems different from other existing technologies;
2. Evaluation of the toxicity of hydrocarbons which may present a potential carcinogenic hazard to the workers;
3. Development of the ability to extrapolate from existing development - pilot scale operations to commercial facilities.

The Modified In-Situ process presents a work situation where on the order of 100 rubblized columns will be in operation at any one time in a commercial facility. This will require simultaneous activities in developing columns for rubblization, while other columns are being fired to produce oil, and other columns are in some stage of shut down or abandonment. This work situation represents a unique condition because of the different potential hazards associated with the different operations, and the presently unknown factors defining releases from in-situ retorts in different states of operation. This

problem deserves special attention to evaluate the magnitude of the potential hazard, and to develop control strategies (involving engineering, administrative, and work practice procedures) to assure adequate worker protection.

In the past industrial hygiene field studies have emphasized the concentration and size characteristics of dusts. This must be expanded to determine the specific chemical composition of the gases and vapors present as a result of each operation, and the potential for these materials to be inhaled, ingested, or result in skin contact to the worker. This will require a more sophisticated sampling and analytical chemistry effort than was performed in past industrial hygiene studies. A major concern will be the varied hydrocarbons associated with different aspects of the unit operations. These data should provide input to toxicological studies.

Existing facilities are inherently one of a kind and ever changing since oil shale technologies are in the development stages. Future operations will probably involve higher levels of automation, more reliable control systems, and more constant operating conditions. An analytical model must be developed to permit extrapolation from data obtained in existing facilities to predict potential exposures in future systems.

V. FUTURE RESEARCH NEEDS

There have been several reports dealing with research needs for health, safety and environmental problems associated with development of the oil shale industry.^{4,13-15} The most recent of these,¹⁴ which is the most detailed, established general and specific research requirements and priorities for various health and environmental related concerns associated with oil shale. Based on these reports, and the previously detailed industrial hygiene and health related concerns associated with development of the oil shale industry, the following ten research priorities are identified below:

1. Analysis of the potential industrial hygiene and safety hazards associated with simultaneous development, operation and abandonment of multiple retorts in a commercial size Modified In-Situ oil shale system. This will require consideration of various aspects of what appears to be a very complex problem. Specifically, the following points must be addressed:

- a) A field sampling program should be initiated as part of the developmental stages of modified in-situ operations to determine the characteristics of the particulates, gases and vapors released during each part of the life cycle of these retorts (i.e., during development, operation, shut down and abandonment). It is likely that data of this type will be site and process specific. Sampling should also attempt to characterize conditions during a typical operating situations.
- b) Establish a strategy for the consecutive development of retorts within limited space confines so as to minimize the potential for worker exposure between adjacent retorts under routine, non-routine and emergency operating conditions.
- c) Evaluate the reliability and effectiveness of engineering or administrative controls used to provide barriers between adjacent Modified In-Situ retorts.

2. Perform field sampling studies to characterize the gases, vapors, and particulates associated with the various unit operations for above-ground retorting. Primary attention should be directed toward the analysis of gases and vapors using analytical procedures such as gas chromatography (GC), high performance liquid chromatography (HPLC), and GC-MS to identify and quantitate specific or classes of hydrocarbons associated with normal and maintenance operations.

These air sampling results should be closely related to the operating conditions in order to facilitate extrapolation to future processes. In all likelihood, data of this type will be process and site specific and considerable attention must be directed toward interpreting the data to permit extrapolation to the next generation of above-ground retorting unit operations.

These data should also be reviewed in light of existing allowable atmospheric concentrations for this industry. Application of the coal tar pitch volatile standard, originally developed for coke ovens, should be reconsidered in light of volatile contaminants associated with oil shale.

3. Data obtained in field studies noted in (1) and (2) should be provided as input to toxicology studies so that the long and short term toxicological effects can be estimated. It seems desirable that

initial toxicology studies should focus on working with complex mixtures which are representative of the material present in the work place and potential exposures atmospheres, rather than working with identified single- or multi-component compounds. For this reason it is critical that the industrial hygiene and toxicology studies be closely coupled. The results of these toxicology studies should be promptly disseminated back to the industrial hygienist, and individuals responsible for operation and design of oil shale facilities.

One potential study which might assist in providing data relating toxicity to retort operating characteristics is the development of an experimental retort to be used in conjunction with animal toxicology studies. This would permit animal exposures under controlled retort conditions. While this will not simulate any one process, it will provide information on the variation in toxicological effects as a function of retort operating parameters.

4. Initiation of a prospective epidemiological study to determine the health effects (if any) associated with working in the oil shale industry. As part of this effort, careful attention should be made to integrating epidemiological data obtained with work activities of the individuals so that the potential or actual exposure of the individual to specific contaminants can be better estimated.
5. Evaluate any special safety problems associated with mining oil shale. This would include roof stability for high roof mines, and the handling of extremely large quantities of waste materials.
6. Evaluate the importance of diesel fumes as a inhalation hazard to miners in the oil shale industry. This problem is not unique to oil shale, however, the synergistic action of diesel fumes with atmospheric contaminants associated with oil shale may present some unique problems.
7. Development of passive air sampling instrumentation for monitoring specific gases and vapors present in significant quantities in the various oil shale unit operations. This sampler development effort should be keyed to those contaminants identified as being the major gases and vapors of concern (based on concentration and potential toxicity as identified by 1, 2, and 3) to oil shale workers.

8. Develop analytical and modeling procedures to permit extrapolation of data and risk assessments obtained from existing oil shale operations to large scale commercial facilities planned for the future. This ability to extrapolate from existing oil shale facilities to future facilities is a critical need to avoid major uncertainties in the future.
9. Initiate laboratory studies to evaluate the effectiveness of existing protective equipment (gloves, air purifying respirators, etc.) for those gases and vapors of major concern in the oil shale industry.
10. Develop an information dissemination system to provide for prompt transfer of information developed by operating personnel, field studies, and laboratory and clinical research activities.

The above ten recommendations are not meant to be all inclusive, and in many instances, are not unique for oil shale. They are presented as a starting point for the panel discussion at this meeting.

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VII. REFERENCES

1. K. W. Crawford, C. H. Prien, L. B. Baboolal, C. C. Shih, and A. A. Lee, "A Preliminary Assessment of the Environmental Impacts from Oil Shale Development," EPA-600/7-77-069; July 1977.
2. C. C. Shih, C. H. Prien, T. D. Nevens, and J. E. Cotter, "Technological Overview Reports for Eight Shale Oil Recovery Processes."
3. Oil Shale and the Environment, EPA-600/9-77-033; October 1977.

4. Environmental Development Plan - Oil Shale FY 1977; EDP/F-01 (77); June 1977.
5. J. Rudnick, L. L. Garcia, G. L. Voelz, and H. F. Schulte, "Paraho Oil Shale Workers Occupational Health," Los Alamos Report (in Press), June 1980.
6. L. L. Garcia and H. F. Schulte, "Air Sampling at Paraho Oil Shale Operations: LA-8032-MS; September 1979.
7. W. D. Holland, "Industrial Hygiene Survey of the Paraho Oil Shale Mining and Processing Facility," PB 265360; September 1976.
8. J. E. Cotter, J. D. Powell, and C. Habenicht, "Fugitive Dust at the Paraho Oil Shale Demonstration Retort and Mine," TRW/DRI/Report for EPA: Draft, March 1979.
9. J. C. Volkwein and P. F. Flink, "Respirable Dust Survey of an Underground Oil Shale Mine and Associated Milling Facility," Bu. M. Info Circular No. 8728; 1977.
10. R. N. Heistand and R. A. Atwood, "Paraho Environmental Data," Draft report by DEI for DOE (EP-78-C-02-4708.A000) February 1979.
11. J. E. Cotter, C. H. Prien, J. J. Schmidt-Collerus, D. J. Powell, R. Surg, C. Habenicht, and R. E. Pressey, "Sampling and Analysis Research Program at the Paraho Shale Oil Demonstration Plant," EPA-600/7-78-065; April 1978.
12. J. Costello, "Health Studies of Oil Shale workers," 11th Oil Shale Symp. Proceed , April 1978.
13. H. F. Schulte, A. K. Stoker, E. E. Campbell, E. C. Anderson, G. E. Dials, "The BER Balanced Program Plan: Oil Shale Technology," LA-6390-MS; June 1976.

14. Mitrex Corp.; Workshop on Health Effects Associated with Oil Shale Development; DOE Contract EP-78-C-01-6203.
15. Environmental Readiness Document - Oil Shale; DOE/ERD-0016, September 1978.